FIELD GUIDELINES FOR COLLECTION, TREATMENT, AND ANALYSIS OF WATER SAMPLES, MONTANA DISTRICT

By J. R. Knapton

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CONVERSION FACTORS

To convert inch-pound units in this report to the International System of units (SI), multiply by the following factors:

Multiply inch-pound unit	By	To obtain SI unit
foot	0.3048	meter
foot per second (ft/s)	0.3048	meter per second
gallon	3.785	liter
inch	25.40	millimeter
ounce (oz)	28.35	gram
pint	0.4732	liter
pound	453.6	gram
pound per square inch (lb/in^2)	6.895	kilopascal
quart	0.9464	liter

Temperatures in degrees Celsius (°C) can be converted to degrees Fahrenheit (°F) by the formula:

$$°F = 9/5\ (°C) + 32$$

FIELD GUIDELINES FOR COLLECTION, TREATMENT, AND ANALYSIS OF WATER SAMPLES, MONTANA DISTRICT

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ABSTRACT

This manual provides a set of standardized guidelines and quality-control procedures for the collection and preservation of water samples and defines procedures for making field analyses of unstable constituents or properties. Seldom is water of such uniformity that a single grab sample is representative of the whole. For this reason a variety of sampler types and sampling methods has been developed.

Descriptions and procedures for field use are given for a number of sampler types. Several methods of sampling are described for which these samplers can be used. Sample-processing devices such as sample splitters and filtration apparatus are discussed along with methods of cleaning. Depending on the type of analysis to be performed in the laboratory, samples may need to be preserved shortly after collection. Various types of preservation are described in detail.

Analyses for unstable constituents or properties are of necessity accomplished in the field. This manual addresses analytical techniques and quality assurance for: (1) Water temperature, (2) specific conductance, (3) pH, (4) alkalinity, (5) dissolved oxygen, and (6) bacteria.

Examples of field report forms are given as attachments. Information pertinent to certain field calculations is also presented.

INTRODUCTION

The purpose of this manual is to set forth guidelines and quality-control procedures for the collection and preservation of water samples and to define procedures for field analyses of unstable constituents or properties. The procedures contained herein are approved for use in water-resources investigations and conform to methods presented in U.S. Geological Survey reports in the series "Techniques of Water-Resources Investigations" (TWRI's) and unpublished technical memorandums.

The development of new and improved field techniques is a continuing process. Therefore, this manual will be updated as necessary. The manual is similar to one prepared by Kister and Garrett (1982) of the Arizona District, modified for conditions in the Montana District. Many of the changes made were to accommodate cold weather conditions.

SELECTION OF GROUND-WATER SAMPLE-COLLECTION SITE

The following discussion is taken from Rainwater and Thatcher (1960, p. 6-7):

> *Ground water is analogous to a surface-water reservoir in that most usable ground water is in motion, although the rate of movement may be very slow and the areal extent very wide. A well can be considered as a sampling point in a large body of slowly moving water, which may differ in chemical composition vertically as well as areally. Most of the forces that cause mixing in bodies of surface water are absent or much weaker in ground-water reservoirs. Turbulence is almost nonexistent. The major forces that tend to mix ground water are probably the differences in velocities as the water moves through material of heterogeneous permeability, pressure differentials and, to a lesser extent, ionic diffusion. The degree of movement induced by pumpage and natural discharge affects the quality. The diversified nature and solubility of the rocks with which the water comes in contact and variations in rate and chemical composition of recharge from precipitation and from the surrounding area tend to make the water heterogeneous.*

Sampling programs are planned to determine the mineral content of the water in the aquifer, although a completely comprehensive answer is not always practical. Efficient collection of water-quality data and intelligent selection of the ground-water sampling site generally require more judicious consideration than the selection of a surface-water sampling site because the elements affecting water quality are not as easily observed.

Because of the diversified purposes of ground-water investigations, it is impractical to issue specific instructions for the selection of sampling sites. Nevertheless, some general ideas can be given. If changes in ground-water quality are not considered in the investigation, there are perhaps two equally satisfactory approaches to the problem of adequate and economical coverage of ground-water quality of an area; both approaches involve the use of comprehensive and partial analyses. The first approach utilizes the determination of key constituents such as conductivity, hardness, and chloride, in a large number of samples collected over the entire area. By this means an areal water-quality pattern may develop that would be a guide in selecting the sites for collection of samples for comprehensive analysis. In the second approach, the key constituents may be unknown at the beginning of the investigation. Therefore, the reverse may be required, and comprehensive analyses may be made on a large number of samples early in the study, and augmented by partial and additional comprehensive analyses of samples from other sites to complete the water-quality picture (Wood, 1976). Either method requires the selection of sampling points from available sites unless the project can support a special drilling program.

In selecting a sampling site to detect water-quality changes, control of the variables that affect the change is important. The hydrologic regimen needs to remain unchanged during an investigation. For example, if irrigation is begun in the vicinity of the well selected as a sampling site to study variations in quality resulting from natural-recharge patterns, the data collected may be essentially of no value.

Although some ground-water studies may be concerned only with surveying the chemical characteristics of the water, the data commonly are used in conjuction with other geologic and hydrologic information. Consequently, the value of the water analysis is usually directly proportional to the facts known about the sources of the sample. One general observation is pertinent: The most useful samples are collected from wells for which additional hydrologic and geologic data are available.

SELECTION OF SURFACE-WATER SAMPLE-COLLECTION SITE

Sampling techniques to be used in a given situation will depend not only on the data needs, but also on the nature of streamflow and other conditions at the sampling site. Ideally, the site will be at or near a streamflow-gaging station because of the need to relate water quality to discharge. The best sample-collection site would be no more than a few hundred feet from the site of the water-stage recorder, unless it has been ascertained that there is no appreciable inflow between the sites. If no gaging station is at or near the sampling site, a discharge measurement will be needed at the time of sampling. Also, if the water-quality station is to be operated throughout the year, some sampling will be done during the winter. Sections of some streams commonly remain open or partly open during the winter. Local residents generally can provide valuable information about ice conditions.

If a sample-collection site is downstream from the confluence of two streams or downstream from a point source of pollution, the collection of a representative sample may require considerable effort because flow from the two streams may not mix readily. If visual observations or field measurements indicate that flow at the sampling site is not mixed, a sufficient number of verticals in the cross section will be needed to provide a representative sample. Selection of a sampling site just upstream from the confluence of two streams also can result in an unrepresentative sample, unless the distance upstream from the confluence is sufficient to minimize backwater effects.

After a sampling site has been selected, samples are collected at the same cross section throughout the period of record, if possible. This does not mean, however, that the same section used during the low-water wading stages must be used during higher stages that require the use of a bridge or cableway.

After the foregoing factors have been considered and a tentative sampling site selected on a perennial stream, field measurements (specific conductance, temperature, pH, and dissolved oxygen where applicable) can be made and documented at several verticals in the cross section to determine the uniformity of the water quality. If the concentrations of suspended sediment or any of the "total" or "total recoverable" chemical constituents (unfiltered sample) are to be determined routinely, samples must be collected from each of several verticals and analyzed individually for suspended sediment (Guy and Norman, 1970). These measurements then could be used by field personnel or the sediment specialist as guides in selecting an adequate number of verticals for obtaining a representative sample.

SAMPLING EQUIPMENT SELECTION AND MAINTENANCE

Planning the field trip and assembling the necessary equipment are essential elements in any program. Provisions need to be made for sampling any condition that might persist, including extreme cold weather and sampling through ice.

The streamflow conditions and sampling structures (bridge, cableway, or other) determine which sampler or samplers are to be used at a station. Stream depths and velocities determine whether hand samplers or cable-suspended samplers are to be used, and the depth-velocity product affects the action of each sampler. The larger the product, the heavier and more stable the sampler required to collect a representative sample.

Stream velocity and depth are factors in determining whether or not a stream can be waded.

[WHEN THE PRODUCT OF DEPTH, IN FEET, AND VELOCITY, IN FEET PER SECOND, EQUALS TEN OR GREATER, A STREAM'S WADEABILITY IS QUESTIONABLE]

However, application of this rule will vary considerably among individuals according to weight and stature and to the condition of the streambed.

If the product of the depth times velocity is greater than about ten, the sampler to use is one that is supported by cable-and-reel equipment. Because the sampler must traverse a path from stream surface to the streambed, the sampler must be heavy enough to resist the drag forces of the flow. A rule-of-thumb is to multiply depth times velocity, then use the sampler whose weight, in pounds, exceeds that product.

Depth-integrating water-sediment samplers

Depth-integrating water-sediment samplers are commonly used and some of their pertinent characteristics and applications are described in the following sections. For a more thorough discussion concerning these and other samplers, field personnel are referred to the report "Field Methods for Measurement of Fluvial Sediment" (Guy and Norman, 1970) and to unpublished Quality of Water Branch Technical Memorandums 76.07, 76.156T, and 77.03. Each of the samplers is identified by the following codes:

US--United States standard sampler.
D--depth integrating.
P--point sampler.
H--hand held by rod or rope; for cable-and-reel suspension the H is omitted.
TM--trace metal; epoxy-coated sampler for the collection of trace metal (minor element) samples.
AL--sampler constructed of aluminum.
BM--bed material.
Q--quart sampler.
XX--last two digits of the year in which the sampler was developed.

For example: a US DH-48 is a depth integrating, hand-held sampler developed in 1948.

Hand-held samplers

Where streams can be waded, or where a low bridge is accessible, one or more of the following samplers can be used, depending on the type of sample.

US DH-48 or US DH-48 TM.--This sampler, including the sample container, weighs 4 1/2 pounds. A standard stream-gaging wading rod is threaded into the top of the sampler body for suspending the sampler. The sampler is calibrated with a nozzle having an inside diameter of one-fourth inch. However, a 3/16-inch nozzle (special order) can also be used. The sample container is a round pint glass milk bottle. The sampler can be used for the collection of all water-sediment samples EXCEPT those for bacteria, oil and grease (O&G), dissolved oxygen (DO), and pesticides where quart samples are required. If the DH-48 sampler is to be used for the collection of pint pesticide samples, the black rubber gasket must be replaced with a silicone gasket. If the sampler is to be used for the collection of trace metals, the metallic nozzle needs to be replaced with a nylon nozzle and the sampler coated with epoxy paint to prevent contamination from metal surfaces (four coats of "Sears Marine"[1] white epoxy, or equivalent).

US DH-75 Q.--This epoxy-coated sampler is a quart version of the wading-type hand sampler. The container is a round quart glass mayonnaise bottle (Owens-Illinois 6762 or equivalent). This sampler can be used for the collection of all water-sediment samples EXCEPT those for bacteria, O&G, DO, and pint suspended-sediment samples.

US DH-59 or US DH-59 TM.--This sampler was designed to be suspended by a hand-held rope in streams too deep to be waded. Because of its light weight (24 pounds), its use is limited to streams having velocities less than about 5 ft/s. The instrument is calibrated and supplied with 1/4-inch, 3/16-inch, and 1/8-inch diameter nozzles. The container is a round pint glass milk bottle. The sampler can be used for the collection of all water-sediment samples EXCEPT those for bacteria, O&G, DO, and pesticides where quart samples are required. If the DH-59 sampler is to be used for the collection of trace metal samples, the black rubber gasket must be replaced with a silicone gasket, the metallic nozzle replaced with a nylon nozzle, and the sampler coated with epoxy paint.

US DH-76 TM.--This epoxy-coated sampler is a quart version of the US DH-59 hand-line sampler. Because of its light weight, its use is limited to streams having velocities less than about 5 ft/s. The container is a quart glass mayonnaise bottle. The sampler can be used for the collection of all water-sediment samples EXCEPT those for bacteria, O&G, DO, and pint suspended-sediment samples.

Tubular Insert Sampler.--This sampler consists of a section of heavy metal tubing (pipe) that will accomodate a sample bottle. The sampler is lowered by rope from a bridge or cableway. Various sampler sizes are available, the most common accommodating 4 oz., 8 oz., and 1-liter sample containers. The sampler is normally restricted to dissolved inorganic constituents when the stream is well mixed. The most common use of the sampler is by field observers in the collection of routine samples for specific conductance. The sampler also has been used during extreme cold when freezing conditions preclude the use of normal type samplers. If used as a replacement during cold weather sampling, all metal parts are coated with epoxy paint (four coats of "Sears Marine" white epoxy or equivalent). In addition, use of the sampler is documented on both the field and the laboratory forms.

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[1] Use of trade names in connection with equipment or supplies in this report is for descriptive purpose only and does not constitute endorsement of the product by the U.S. Geological Survey.

Cable-and-reel samplers

When streams cannot be waded but are less than about 15 to 20 feet deep, one of the following reel-type samplers can be used for obtaining depth-integrated water-sediment samples.

US D-49 or US D-49 TM.--This 62-pound sampler was designed for sampling with a cable-and-reel suspension. The sampler is attached to the cable with a standard hanger bar. The instrument is supplied with 1/4-inch, 3/16-inch, and 1/8-inch nozzles. The sample container is a round pint glass milk bottle. The sampler can be used for the collection of all water-sediment samples EXCEPT those for bacteria, O&G, DO, and pesticides where quart samples are required. If the D-49 sampler is to be used for the collection of trace metal samples, the black rubber gasket needs to be replaced with a silicone gasket, the metallic nozzle replaced with a nylon nozzle, and the sampler coated with epoxy paint.

US D-74 or US D-74 TM.--This 62-pound reel-type sampler is a quart version of the D-49 sampler. The sampler will accommodate either a quart glass mayonnaise bottle or a round pint glass milk bottle. When the pint bottle is used, an adapter provided with the sampler is inserted inside the bottle cavity. The sampler can be used for the collection of all water-sediment samples EXCEPT those for bacteria, O&G, and DO. If the D-74 sampler is used for the collection of pesticide samples and trace metal samples, the black rubber gasket is replaced with a silicone gasket, the metallic nozzle replaced with nylon nozzle, and the sample coated with epoxy paint.

US D-74 AL.--This reel-type 40-pound sampler is an aluminum version of the D-74 sampler. The sampler can be used for the collection of all water-sediment samples EXCEPT those for bacteria, O&G, and DO. If the sampler is to be used for the collection of pesticide samples and trace metal samples, the black rubber gasket is replaced with a silicone gasket, the metallic nozzle replaced with a nylon nozzle, and the sampler coated with epoxy paint.

US P-61 TM.--This 105-pound reel-type sampler with a 3/16-inch nozzle was designed as a point-integrating sampler but also can be used as a depth-integrating sampler in streams too deep or too swift to use other samplers. The sampler can be used for depth integration (in 30-foot increments) to total stream depth of 180 feet using a 1-pint container.

The sampler is designed for suspension from a steel cable having an insulated inner conductor core. By pressing a switch located at the operator's station, a current is supplied through the cable to a solenoid in the sampler head by storage batteries connected in series to produce 24 to 48 volts. If the suspension cable is longer than 100 feet, a larger voltage may be required. When the solenoid is not energized, the valve is in the nonsampling (closed) position. When the solenoid is energized, the valve is in the sampling (open) position. The sampler will accommodate either a quart glass mayonnaise bottle or a pint glass milk bottle. When the pint bottle is used, an adapter must be inserted into the bottle cavity. The sampler can be used for the collection of all water-sediment samples EXCEPT those for bacteria, O&G, and DO.

This sampler can be used in streams where depths exceed 20 feet and where the combination of depth and velocity cause other samplers to overfill at the maximum allowable transit rate. Stream depths of as much as 30 feet can be accommodated with the P-61 TM sampler by integrating the depth in only one direction at a time. Generally, the sampler is first lowered to the streambed (with the intake closed), and the depth determined and the transit rate estimated. Upward integration from the bottom is maintained at a given transit rate immediately on opening the intake nozzle. For precise sampling, a second bottle in the same vertical is collected on a descending trip.

Depths of as much as 60 feet can be sampled by using a modification of this procedure. First the closed sampler is lowered to the bottom and the depth noted. The nozzle is opened and the sampler raised at the predetermined transit rate to an even foot at about half the depth. At this point, the nozzle is closed immediately and the sampler is raised to the surface. After retrieving the sample, a clean bottle is inserted and the sampler is lowered to that depth where the nozzle was closed on the initial ascending trip. At this point, the nozzle is opened and the upper half of the depth is sampled as the sampler is raised at the identical transit rate used for sampling the lower half of the depth. For precise sampling, third and fourth bottles are used on descending trips. Depths greater than 60 feet can be sampled using more steps in the procedure as needed.

Sampler nozzles and gaskets

Each water-sediment sampler is equipped with a set of different sized nozzles. The reason for nozzles of various sizes is that stream velocities and depths may be great enough to cause the bottle to overfill for a specific transit rate when using the largest nozzle. To reduce the quantity of sample entering the bottle and to prevent overfill, the next smaller diameter nozzle is used. However, the best sample is obtained with the largest nozzle that can be used in a given situation. Because each of the sampler nozzles is calibrated for its particular sampler or series of samplers, a nozzle from one series of samplers is not used in another series of samplers. Exceptions: The following nozzles are interchangeable--DH-59 with DH-76, and D-49 with D-74.

Except for samplers of the US DH-48, US DH-75, and US P-61 series, those samplers described previously are equipped with three different diameter nozzles--1/4-inch, 3/16-inch, and 1/8-inch. The US DH-48 and US DH-75 samplers were designed for use in slow wadeable streams; therefore, the sampler has not been calibrated for a 1/8-inch nozzle. The US P-61 sampler is supplied only with a 3/16-inch nozzle because the opening through the valve mechanism is only 3/16-inch in diameter.

Of equal importance to using the correct diameter nozzle is the necessity to use the proper gasket to seal the bottle mouth sufficiently. Each sampler series uses a different size or shaped gasket.

Any of the samplers used for the collection of pesticide and trace metal samples needs to be equipped with the appropriate nylon nozzles and silicone rubber gaskets. Nylon nozzles are color coded as follows:

Samplers	Color
DH-48	Yellow
DH-59	Red
D-74 and D-49	Green
P-61	Blue

Special care is needed in tightening nylon nozzles into a sampler having a teflon nozzle plug. Nozzles are tightened only by hand. The teflon plug is a friction fit and will be damaged by wrench tightening.

Before departing on a field trip, personnel are to assure that the samplers are in good working condition. Nozzles, gaskets, and air exhausts are checked and replaced when necessary. Nozzles or exhausts might be plugged; nozzles or gaskets might be damaged; and the epoxy coating might be chipped. The flow system of the sampler can be checked for plugging or leaks by blowing through the nozzle with a bottle in the sampler. Use a short length of rubber tubing to blow into the nozzle because of the possibility of previous contamination by polluted water. If air does not circulate easily, check the nozzle to ensure that it is clear and remove and clean if necessary. If the air exhaust is plugged, it usually can be cleared with a flexible piece of multistrand wire. To check the gasket for adequate seal, insert a bottle in the sampler, close the air-exhaust port with a finger, and blow through the sampler nozzle. If air escapes around the bottle mouth, the gasket may be defective or worn or the spring-loaded foot that holds the bottle in place might not be working properly.

Biochemical oxygen demand (BOD) samplers

The BOD sampler accommodates a glass BOD bottle having a volume of 300 mL (milliliters); it is designed to provide for a threefold displacement of water in the sample bottle without aeration. This 10- to 15-pound metal sampler is used for the collection of unaerated samples for the measurement of dissolved oxygen during weather conditions that make in situ measurements impractical. If velocity of the flow is too great for the sampler to be lowered to the streambed without aeration, sounding weights are attached to the rope or cable from which the sampler is suspended.

Bed-material samplers

The samplers commonly described in this section are physically limited to the collection of bed-material samples consisting of particles finer than about 30 or 40 mm (millimeters) in diameter (finer than medium gravel).

Hand-held sampler--US BMH-60

The US BMH-60 sampler is a 30-pound hand-line sampler designed to sample streams having moderate depths and velocities and whose bed material is moderately firm but contains a minimum amount of gravel. The sampler mechanism consists of a scoop or bucket operated by a spring. The scoop when activated by release of tension on the hanger rod can penetrate into the bed about 43 mm and can hold approximately 175 cm^3 (cubic centimeters) of material.

To cock the bucket into an open position for sampling, the sampler must first be supported by the hand line; then the bucket can be opened with an allen wrench. The hanger rod to which the hand line is attached is grooved so that a safety yoke can be placed in position to maintain tension on the rod assembly and to hold the bucket open for cleaning.

[CAUTION MUST BE USED WITH THIS SAMPLER AND AT NO TIME ARE THE HAND OR FINGERS TO BE PLACED IN THE BUCKET OPENING. ACCIDENTAL CLOSING OF THE BUCKET COULD CAUSE PERMANENT INJURY]

The bucket closes when the safety yoke is removed and tension on the hand line is released as will occur when the sampler comes to rest on the streambed.

Cable-and-reel sampler--US BM-54

The US BM-54 is a 100-pound cable-and-reel sampler designed to sample bed material of a stream of any reasonable depth, except for streams with extremely large velocities. Operation of the sampler is similar to the US BMH-60 in that it takes a sample when tension on the cable is released as the sampler touches the bed.

The sampler needs to be equipped with a safety bar that can be rotated over the front or cutting edge of the bucket when cocked into open position.

[LIKE THE BMH-60 SAMPLER, CAUTION MUST BE USED WHEN WORKING WITH THE BUCKET. HANDS AND FINGERS ARE NOT TO BE PLACED IN THE BUCKET OPENING]

The driving force of the bucket is a coil-type spring. The tension on the spring is adjusted by the nut-and-bolt assembly protruding from the front of the sampler. Maximum tension need be used only when the streambed material is very firm.

Support equipment

Much of the equipment used in stream-gaging procedures is also used as support equipment for handling of water-sediment and other type samplers. A discussion of the various types of support equipment is beyond the scope of this manual. However, some of the support equipment is listed below. For a discussion of these and other equipment, field personnel are referred to the report "Measurement and Computation of Streamflow" by Rantz and others (1982).

1. Cranes
    a. Type A--designed for weights of 150 pounds or less.
    b. Type D--designed for weights of as much as 200 pounds.
2. Crane bases
    a. Four-wheel base--always used when type D cranes are used and when 75-, 100-, and 150-pound weights are used with the type A crane.
    b. Three-wheel base--can be used with type A crane.

3. Reels
   a. Type A--has a fixed crank and no brake. Will accommodate 80 feet of 0.10-inch cable.
   b. Type B--has a brake and two interchangeable handles. Will accommodate 125 feet of 0.10-inch cable.
   c. Type D--has a brake and two cranks for 2-person operation. Will accommodate 200 feet of 0.10-inch cable.
   d. Type E--has a brake and two cranks for 2-person operation. Will accommodate 175 feet of 0.10-inch cable (the selection of the type of reel is based largely on the maximum length of the cable that is required).
4. Hanger bars, connectors, and pins--for connecting to cable and reel.
5. C-type weights--15-, 30-, 50-, 75-, 100-, and 150-pound weights as applicable.
6. Tag-lines--for measuring distances and widths.
7. Stop watch.
8. Ropes--for suspending hand-line samplers.
9. Waders.
10. Assortment of safety equipment such as cones and signs.
11. Wading rod.
12. Gage-house keys.
13. Cable-car puller.
14. Tools.
15. Flashlight.

Methods of cleaning samplers and sample-processing equipment

[SAMPLES ARE TO BE PROTECTED AGAINST CONTAMINATION AT ALL
TIMES. AS PART OF QUALITY ASSURANCE, SAMPLERS AND SAMPLING
EQUIPMENT ARE TO BE
THOROUGHLY CLEANED PRIOR TO USE]

The critical parts of depth-integrating water-sediment samplers are the nozzle, that part of the sampler head underneath the gasket, and the entire center part of the sampler head that may contact the sample. The sampler is cleaned with a moderate amount of low-phosphate detergent (Alconox) solution and washed with tap water prior to the field trip and in the field after sampling a particularly "dirty" site. The use of excessive quantities of detergent is discouraged to avoid possible contamination of the nutrient sample. If the sampler is to be used for the collection of samples for pesticide analysis, the sampler is rinsed with hexane before the rinse with tap water.

Upon arriving at each field site prior to sampling, field personnel are to thoroughly rinse the empty sampler in the stream to remove any contaminant.

Prior to the field trip, the BMH-60 sampler to be used for the collection of bed material for pesticide analysis is cleaned as follows:

1. With the bucket in the closed position, remove the two large flathead screws and the socket-head capscrew at the downstream edge of the bucket.

2. Insert the allen wrench in the shaft, open the bucket about one-third of the way, and remove the cover plate-gasket-base plate assembly.

3. Open the bucket fully and insert the safety yoke.

4. Using a stiff long-handle brush, clean the bucket throughly with detergent, hexane, detergent again, and tap or deionized water.

5. Clean the cover plate-gasket assembly with detergent, hexane, and tap or deionized water.

6. Reassemble the sampler and keep bucket closed until ready for sampling.

Upon arriving at each field site and prior to sampling, rinse the sampler with native water.

The U.S. Geological Survey churn splitter, which is used for compositing and splitting water-sediment samples, is cleaned prior to the field trip as follows:

1. If the churn is to be used for compositing trace metal samples, soak for about 4 hours with a 5-percent solution of hydrochloric acid. (If churn splitter is not to be used for trace metal samples, omit this step.)
2. Clean with low-phosphate (Alconox) detergent.
3. Rinse with tap water
4. Rinse with deionized water.

Cleaning of the churn in the field between individual sampling sites can be accomplished by rinsing with deionized water immediately after sampling is completed at each site. At the next site, rinse with native water.

Unless special instructions are available, collection bottles used in the various samplers for chemical analysis are to be cleaned prior to the field trip in the same manner as the churn splitter. Also the same procedure is used in the field between individual sampling sites. An extra set of clean sample bottles is to be carried in case of breakage or loss.

The filtration apparatus is flushed with distilled water after each use. The used filter membrane is removed and the screens and plates rinsed copiously with distilled water. Screens are not to come in contact with one another and are to remain in their original top or bottom position. During periods of non-use a filter membrane or a filter divider is placed between the screens. The attached intake and outlet teflon hoses are protected from contamination during nonuse by inserting the ends in plastic bags ("whirlpaks"). The plates and screen can be periodically cleansed by using alternate baths of chlorox and 5-percent hydrochloric acid. A glass pie plate with 1/4-inch depth of cleaning solution can be used as a bath.

Sampling of a particularly dirty site may require that sampler and churn splitter be thoroughly cleaned in the field. Thus, field vehicles are to be equipped with the following material:

1. Low-phosphate (Alconox) detergent
2. Deionized or distilled water
3. Hexane detergent
4. Stiff long-handle brush

SAMPLE COLLECTION AND TREATMENT

General considerations

Many of the dissolved ions normally present in natural waters may be lost from the water sample before it is analyzed in the laboratory because of such chemical and physical reactions as oxidation, reduction, precipitation, adsorption, and ion exchange. Therefore, some properties or constituents such as specific conductance, temperature, dissolved oxygen, alkalinity, and bacteria may change dramatically within a few minutes or hours after sample collection. Immediate analysis in the field is required if accurate results for these parameters are to be obtained. Samples for other constituents may be stabilized by preservative treatment. Some examples of preservative treatment are refrigeration to minimize chemical and biological change due to biologic activity and the addition of acid to prevent the precipitation of cations.

Analysis for "total recoverable" and "total" constituents requires a raw (unfiltered) sample of the water sediment mixture; analysis for "dissolved" constituents requires a filtered sample (generally, through a 0.45 micrometer membrane filter). Other analyses may require bottom material, residue of a filtered sample, or biological material obtained on an artificial substrate. The type of sample treatment required is designated by the U.S. Geological Survey Central Laboratory and defined in their "Service Catalog." Specified sample containers also are listed. Preservatives and bottles are available upon request from the Central Laboratory. Policies of contract laboratories may differ somewhat regarding preservatives and sample containers.

Samples are to be shipped from the field to the laboratory with no delay--preferably the day they were collected. An exception might be when samples are collected near the end of the week and there is reason to believe the shipment will arrive and be held in the Post Office over the weekend. In such instances the nutrients, and other samples requiring cooling, must be held in a dark, refrigerated condition. Another exception to the immediate shipment of samples involves daily samples collected by field observers for the analysis of specific conductance. For practicality, these samples are shipped to the District Laboratory on a monthly basis.

Methods of ground-water sampling

The unstable nature of many chemical and physical properties in ground water requires special collection procedures for samples. In addition, the geochemical controls and nature of the aquifer system may further complicate the method by which samples are collected. The following are general guidelines to use in collection of samples from springs and wells. More detailed information can be found in Wood (1976).

Sampling from springs

For sampling springs in unconsolidated deposits, a well point or slotted pipe can be driven into the ground to a depth of 1 meter or less adjacent to the spring. If the flow is not artesian, the sample can be collected using a small pitcher pump. Plastic pipe and plastic well screen are used for trace metal samples. To sample large upwelling springs, submersible electric pumps placed at the mouth of the spring by hand or attached to a pole generally work well. When sampling for trace metals, plastic is used for the pump housing, pump impellers, and tubing.

Sampling from wells

Wells are pumped prior to sampling to ensure that stagnant water is flushed from the system and the sample is representative of water in the aquifer. Samples are not collected until temperature, specific conductance, and pH remain at constant values. The sample is collected near the wellhead before the water has gone through pressure tanks, water softeners, or other treatment. When wells are not equipped with pumps, a submersible pump with an outside power source is preferred. A pitcher pump may be used if the water level is within about 7 meters of the surface. If pumping cannot be done, a small-diameter point sampler can be used, but only after the well has been bailed until temperature, specific conductance, and pH are constant. Bailers and point samplers usually contaminate the sample with oxygen.

Well packers can be used to sample from individual aquifers tapped by multiscreen or open-hole wells receiving water from several aquifers. Such wells often are avoided in sampling for geochemical studies because of greater costs involved in the use of packers.

Methods of surface-water depth-integrating sample collection

Proper sampling techniques are important to ensure that a sample is representative of the flow in the cross section. The most complete discussion of sampling techniques is found in the report "Field Methods for Measurement of Fluvial Sediment," (Guy and Norman, 1970). Some aspects of sampling are included also in other Geological Survey Techniques of Water-Resources Investigations manuals (see list of references) and quality of water technical memorandums (unpublished).

The number of verticals to be sampled at a site relates primarily to the collection of a representative sample in the cross section and secondarily to the volume of the sample required. With few exceptions, samples that are to be analyzed for suspended sediment or total recoverable constituents need to be collected by using water-sediment, depth-integrating samplers. Instances where use of these samplers are not required are as follows:

1. Extreme low flow where the use of the sampler is impractical. Samples may be collected by immersing the bottle by hand (dip).

2. Under extreme cold temperatures when freezing conditions preclude the use of the normal sampler. In such instances the tubular insert sampler is used. To the degree that is possible, sampling methodology is to be compatible with that used with other type samplers; that is, depth integration and multiple verticals.

3. Samples collected for dissolved chemical constituents that are well mixed within the section. If field measurements of specific conductance show the water to be well mixed, a sample obtained at a single vertical near the centroid of flow may be assumed to be representative of the total flow.

4. Collection of sterile aseptic samples for bacteria work. These samples may be collected at midstream by hand dipping if the stream is wadeable, or otherwise by using the tubular insert sampler with a sterile sample container inserted.

Samples collected at remote sites by automatic samplers need to be retrieved at the earliest possible time. Samples collected in this manner will be analyzed only for constituents that do not require onsite preparation and will be assumed to be representative of that particular flow event. Except for suspended sediment, an aliquot from each bottle collected will be composited to form one sample per event; the appropriate begin and end dates and times for the flow event will be entered into storage, thus indicating a composite sample of the event. When possible, adequate cross-section samples are to be obtained and analyzed for nutrients, bacteria and other scheduled constituents such as suspended organic carbon (SOC), total organic carbon (TOC), and dissolved organic carbon (DOC).

Samples collected by automatic samplers for suspended-sediment concentrations will be analyzed individually and the specific conductance will be measured for each sample. Cross-section samples are to be collected at appropriate intervals, using either the equal-discharge-increment (EDI) method or the equal-width-increment (EWI) method to obtain cross-section coefficients. The coefficients are then applied to the concentration determined at a single vertical to obtain a value that is representative of the average concentration in the cross section.

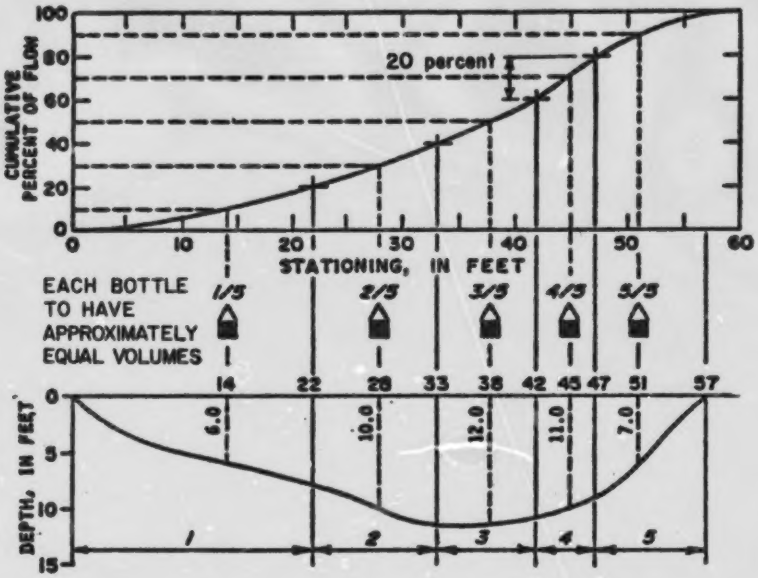
If a representative sample can be obtained by sampling at one vertical, then obtain the volume of sample required at one vertical near the centroid of flow. However, if samples are to be collected at a single vertical for suspended sediment or any of the total or total recoverable chemical constituents, sufficient data must be available to document that materials suspended in the flow are uniformly distributed throughout the cross section. If such data are not available or if flow conditions dictate that suspended materials are not uniformly distributed throughout the cross section, multiple verticals need to be sampled using either the EDI method or the EWI method.

EDI method of sampling for suspended sediment, total recoverable and dissolved chemical constituents, and phytoplankton

The EDI method, in which samples are obtained at the centroids of equal discharge increments, is usually limited to streams having stable channels where discharge rating curves vary little during a year. This method requires that field personnel have knowledge of the streamflow distribution in the cross section before sampling verticals can be selected. If such information can be obtained, the EDI method can save time and labor over the EWI method, especially on larger streams, because fewer verticals are required. To select sampling verticals for the EDI method when prior knowledge of the flow is available, graphs of cumulative discharge in percent of total discharge versus distance from the left or right bank are prepared for low-, medium-, and high-flow conditions for the site. For streams where the EDI method is applicable, these graphs are used as sampling instructions that can be kept in the shelter at the site and in the field vehicle.

The number of equal-discharge increments required to divide the cross section will depend on the size of the river and will generally range from 4 to 10 (fig. 1).

Sampler D-49: nozzle size 3/16-inch ID. Stream width 57 feet; maximum stream depth 12 feet; maximum velocity, 5.0 feet per second; width of section containing 20 percent of flow; variable, 5 to 22 feet; 20 percent of flow per section will give five sampling verticals; transit rate (from nomograph) variable, 0.3-2.0 feet per second.



[ft, feet; ft/s, feet per second; s, seconds]

Increment No.	Percent discharge	Increment width (ft)	Increment depth (width)	Velocity (ft/s)	Maximum transit rate (ft/s)	Transit rate[1] (ft/s)	Total transit time[1] (s)
1	20	22	6	2.0	1.2	0.3	42
2	20	11	10	4.0	1.6	1.1	14
3	20	9	12	5.0	2.0	1.6	9
4	20	5	11	4.0	1.6	1.2	13
5	20	10	7	3.0	1.2	.6	25

[1] Using pint sample container and filling to about 85 percent of capacity

Figure 1.--The equal-discharge-increment (EDI) sampling method.

The initial selection of parts into which the cross section is to be divided for the EDI method is not governed by any predetermined number of sampling points, but rather is chosen on the basis of the following:

1. A discharge measurement is made at the cross section where sampling is to be done. From this measurement, a graph can be constructed using cumulative percent discharge plotted against cross-section stationing. If the cross section is stable, the graph may be used to determine sampling points without having to make a discharge measurement. However, this graph needs to be verified occasionally with computations from recent discharge measurements. Commonly a series of discharge measurements representing low, medium, and high flows is plotted on a single graph and used throughout the range. An example of this type of graph is shown as figure 2.

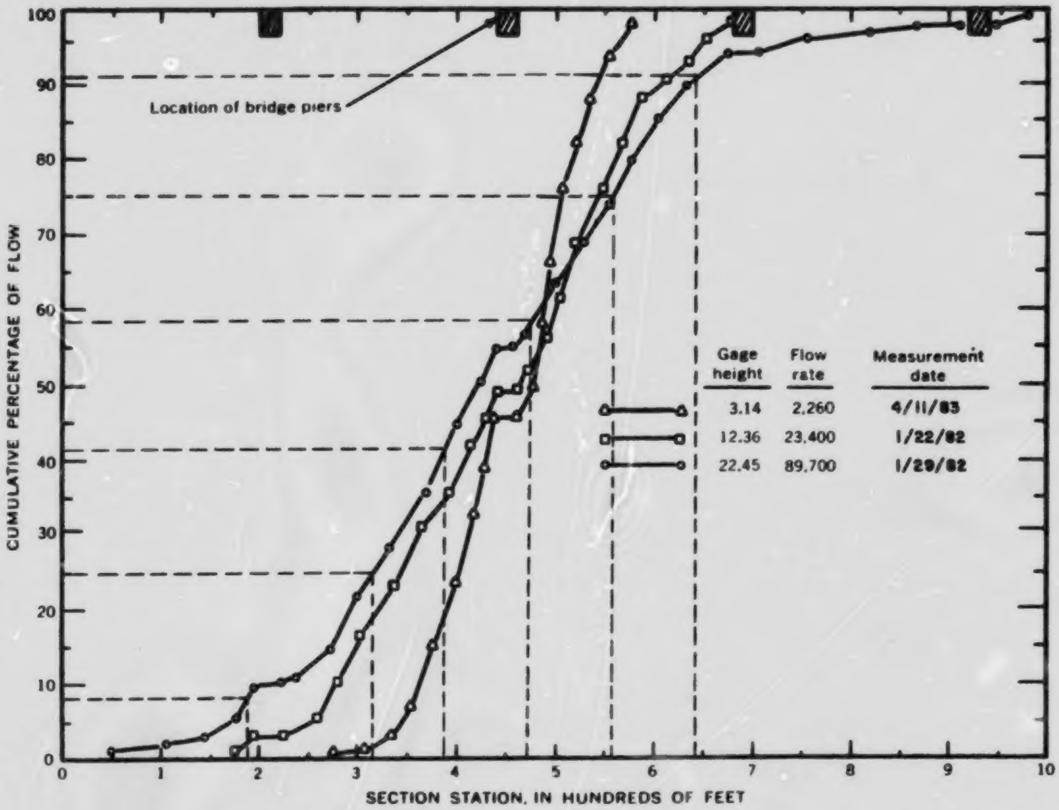


Figure 2.--Cumulative percentage of the total water discharge for three rates of flow with distance across the stream section. Broken lines indicate the stationing of centroids for six eqaul-discharge increments during high flow. Gage height in feet; flow rate in cubic feet per second.

2. A visual inspection of the cross section is made noting the location, if any, of still-water areas or filaments of faster than normal flow, and piers or other obstructions. Cross-sectional surveys of specific conductance, temperature, pH, and dissolved oxygen are made on a seasonal basis to determine if mixing is a problem.

3. Based on the information from the discharge measurement, the visual inspection of the cross section, previous cross sectional surveys, and other information such as laboratory considerations, the decision is made, usually in the relatively calm atmosphere of the office, as to the number of parts needed to adequately define the concentration of suspended sediment in transport through the cross section. The larger the variability in the section and the larger the stream, the more increments will be selected. The final decision as to the number of increments will rest with the District Water Quality Specialist.

Using the EDI method, samples are then collected at the center of each increment of flow as determined from a streamflow measurement or from a cumulative discharge graph. Each bottle is filled to no more than 3 inches from the top. Overfilling can cause secondary circulation, resulting in enrichment of heavy particles in the sample that is not representative of the water-sediment mixture flowing down the stream. Care is needed not to bump the sampler against the streambed causing bed material to rise and enter the bottle. Each bottle is visually inspected; if found to contain excess amounts of large particles, it is emptied, rinsed, and refilled.

[BECAUSE BOTTLES REPRESENT EQUAL PORTIONS OF FLOW, EACH BOTTLE MUST CONTAIN APPROXIMATELY EQUAL VOLUMES OF WATER-SEDIMENT MIXTURE]

The length of immersion time of the sampler can be determined from figure 3. General guidelines for the EDI method of sampling are as follows:

1. Determine the number and locations of verticals to be sampled on the basis of flow conditions and the volume of water needed for analysis. For many streams about four to eight verticals will be sufficient. For example, if six verticals are selected, each of the verticals (stations) needs to be at the centroid of 16.7 percent increments of the discharge--that is, at stations of cumulative discharges of 8.3, 25, 41.7, 58.3, 75 and 91.7 percent. If any of the stations selected are at or near bridge piers or other obstructions where turbulence interferes with the streamflow lines, the sampling station is to be moved a sufficient distance from the obstruction to minimize the effects of the turbulence.

2. After the locations of the sampling stations have been determined, select and assemble the proper sampling and support equipment and safety equipment, such as cones and signs.

3. Read and record the gage height and time at which sampling is begun.

4. Move sampling and support equipment to first station to be sampled.

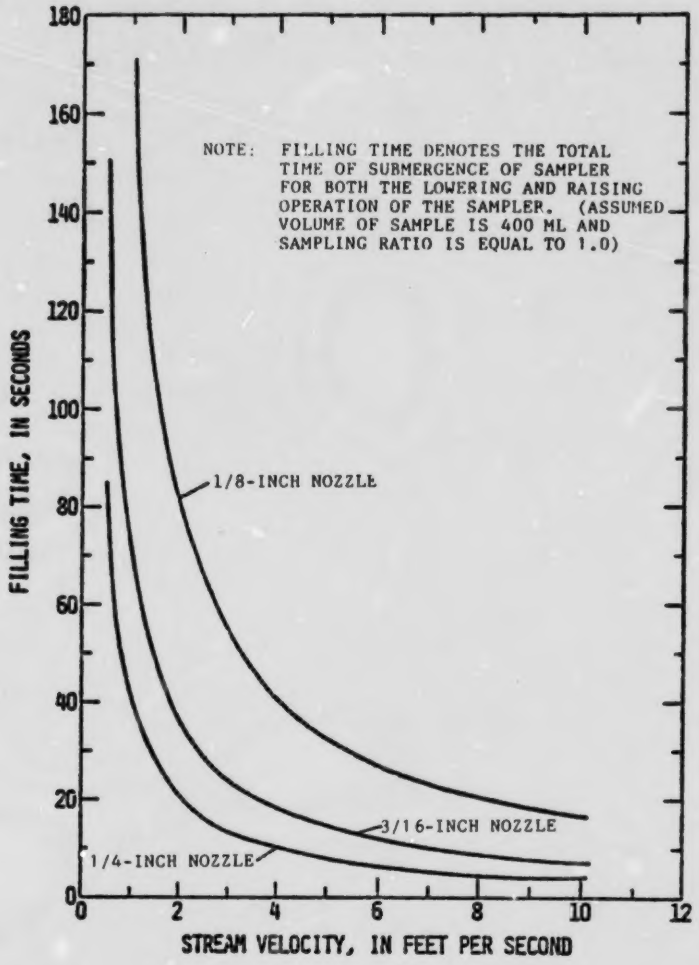


Figure 3.--Time for a suspended-sediment sample bottle of 1-pint capacity to be filled to about 85 percent of capacity.

5. Estimate the sampler transit rates and times from the depths and velocities of flow in each vertical. The transit rate in a vertical needs to be kept constant throughout at least a single direction of travel in that vertical when using the EDI method. The relationship between stream velocity and corresponding filling time (time of submergence of the sampler) for both the pint and quart bottles is shown in figures 3 and 4. A nomograph is given in figure 5 for which the average sampler transit rate and filling time can be determined, given the depth of the vertical and the mean velocity of flow in the vertical.

6. If concentrations of suspended sediment and chemical constituents are to be determined for the stream, collect from each vertical a separate 1-pint

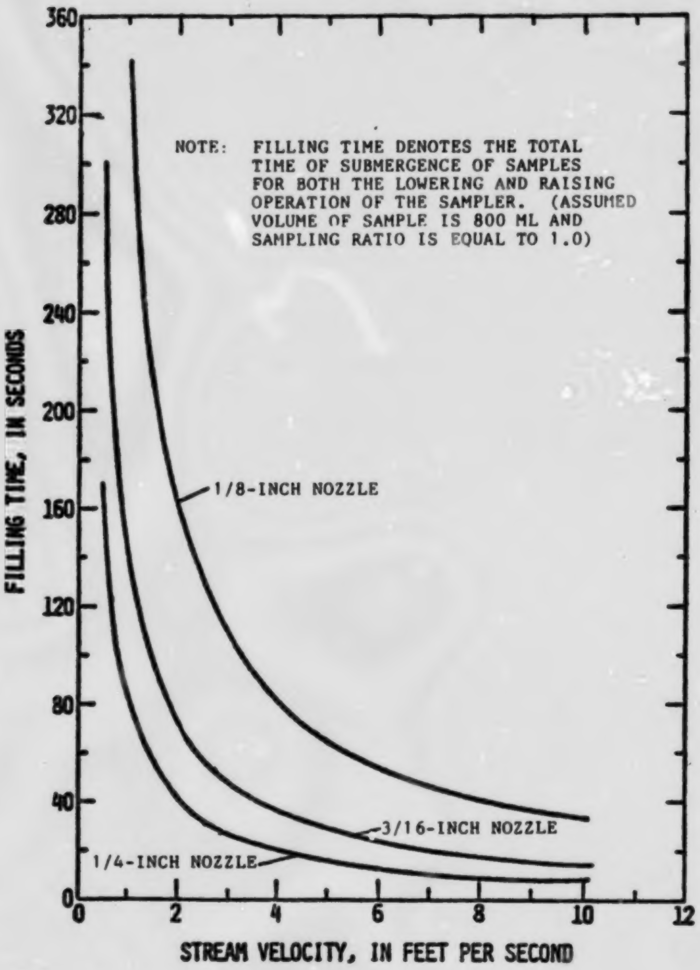
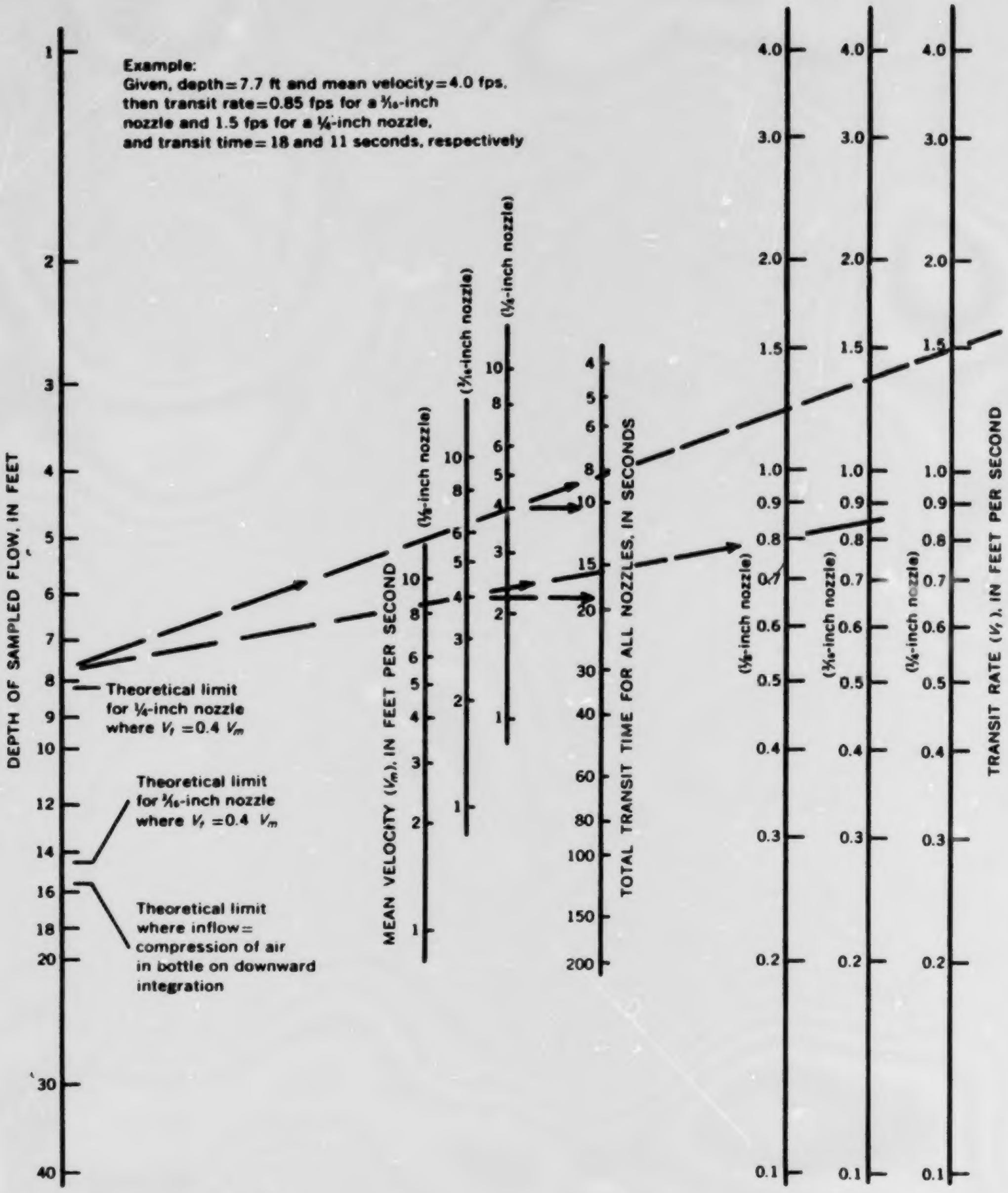


Figure 4.--Time for a suspended-sediment sample bottle of 1-quart capacity to be filled to about 85 percent of capacity.

sample for suspended sediment and 1-pint or 1-quart samples for chemical constituents. The same pint or quart glass bottle is used for each vertical in the cross section for chemical constituents. (Swirl the pint or quart sample gently to keep sediment suspended and pour into churn after sampling each vertical).

[THE INDIVIDUAL DEPTH-INTEGRATED SAMPLES FOR THE DETERMINATION OF DISSOLVED OR TOTAL CHEMICAL CONSTITUENTS (EXCEPT THOSE FOR TOC, DOC, SOC, O&G, BACTERIA, AND PESTICIDES) ARE TO BE COMPOSITED IN THE CHURN SPLITTER]



Example:
Given, depth = 7.7 ft and mean velocity = 4.0 fps, then transit rate = 0.85 fps for a 3/16-inch nozzle and 1.5 fps for a 1/4-inch nozzle, and transit time = 18 and 11 seconds, respectively

ROUND TRIP (STREAM SURFACE TO BED AND RETURN) SUSPENDED-SEDIMENT SAMPLER TRANSIT RATE AND TRANSIT TIME FOR 1/8-, 3/16-, AND 1/4-INCH INTAKE NOZZLES, GIVEN THE SAMPLING DEPTH AND MEAN VELOCITY OF FLOW.

Figure 5.--Sampler transit rate and transit time for a 1-pint sample container to be filled to about 85 percent of capacity.

The volume of the sample collected at a vertical is dependent primarily upon the stream velocity and the depth. Because the operator has no control over these factors, the volume of the sample is regulated by selecting a nozzle of appropriate size or by varying the total time of submergence of the sampler. However, the operator has the option of making any number of up and down trips in each vertical.

7. If either the pint or quart container becomes completely filled during a sampling operation, discard the sample, as it will not be representative, and collect another sample.

8. Label each of the pint samples for suspended sediment analysis with the following information:

   a. Station number, name, and location of the stream.
   b. Date.
   c. Mean time and gage height (or discharge) for the period of sample collection (after step 10).
   d. Sampling location (location in the vertical section).
   e. Water temperature.
   f. Initials of sample collector.

9. Read and record the gage height and time at which sample collection was completed.

10. Calculate and record on the field notes the mean time and gage height for the period of sample collection.

11. Complete field measurements, filtration, and preservation of samples as applicable.

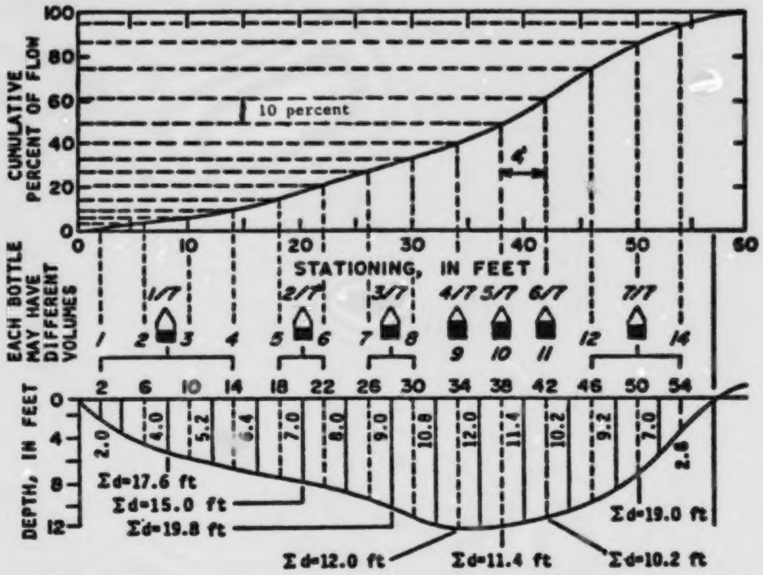
12. Disassemble and clean samplers as described in the section "Methods of Cleaning Samplers and Support Equipment."

EWI method of sampling for suspended sediment, total recoverable and dissolved chemical constituents, and phytoplankton

On wadeable streams and any stream that is subject to a shifting channel, sampling is generally easiest using the EWI method, formerly called ETR or equal-transit-rate method. A shifting channel makes it impossible to establish a set of percentage-discharge curves applicable from one visit to the next. Thus, if a water-discharge measurement is not made immediately before collection of water-sediment samples at these sites, the EWI method is to be used.

The EWI method requires equal spacing of several verticals across the cross section (fig. 6) and an equal transit rate, both up and down, in all verticals. In the EWI method, the width of the stream is determined by reference to a tagline across the stream or to the markings on a bridge rail or a cableway. The stream width is then divided into a number of intervals of equal width, the number of intervals being dependent on channel width, apparent uniformity of lateral sediment distribution, and depth and velocity distribution across the stream.

Sampler D-49; nozzle size 1/4-inch ID; width 57 feet; maximum depth 12 feet; average velocity, 3.5 feet per second; width of section containing 10 percent of flow at deep fast section 4.0 feet; 4 feet wide sections will give 14 sampling verticals; transit rate (3.5 ft/s x 0.4) 1.4 feet per second.


CUMULATIVE PERCENT OF FLOW
0
20
40
60
80
100
10 percent
4'
0
10
20
30
40
50
60
STATIONING, IN FEET
EACH BOTTLE MAY HAVE DIFFERENT VOLUMES
1/7
2/7
3/7
4/7
5/7
6/7
7/7
1
2
3
4
5
6
7
8
9
10
11
12
14
2
6
10
14
18
22
26
30
34
38
42
46
50
54
DEPTH, IN FEET
0
4
8
12
2.0
4.0
5.2
6.4
7.0
8.0
9.0
10.8
12.0
11.4
10.2
9.2
7.0
2.8
Σd=17.6 ft
Σd=15.0 ft
Σd=19.8 ft
Σd=12.0 ft
Σd=11.4 ft
Σd=10.2 ft
Σd=19.0 ft

Sampling vertical No.	Percent of flow	Station No.	Width of increment (ft)	Transit rate (ft/s)	Percent of sample
1	2	2	4	1.4	--
2	4	6	4	1.4	--
3	6	10	4	1.4	--
4	10	14	4	1.4	16.6
5	16	18	4	1.4	--
6	22	22	4	1.4	14.2
7	28	26	4	1.4	--
8	34	30	4	1.4	18.7
9	42	34	4	1.4	11.3
10	50	38	4	1.4	10.8
11	62	42	4	1.4	10.2
12	76	46	4	1.4	--
13	88	50	4	1.4	--
14	96	54	4	1.4	18.2

Figure 6.--The equal-width-increment (EWI) sampling method.

The intervals used in EWI sampling are not selected on any predetermined number of sampling points, but rather on the basis of the following: 1) Visually inspect the stream from bank to bank, observing the velocity and depth distribution as well as apparent distribution of sediment in the cross section, 2) determine the size of interval that represents approximately 10 percent of the flow at that part of the cross section where the "unit width discharge" is largest or the greatest concentration of sediment is moving. This interval size must then be used for the ENTIRE EWI cross section and will govern the number of intervals used. The number of sections is generally not less than 10 nor more than 20.

Sampling verticals are at the center of the selected intervals unless obstructions such as piers are present. For example, in a stream 57 feet wide that has been divided into 14 intervals of 4 feet each, the first sampling vertical would be 2 feet from the water's edge and subsequent verticals would be at 6 feet, 10 feet, 14 feet, and so forth, from the starting point water edge. Even if the flow is divided, as in a braided channel, the sampling intervals must be identical from channel to channel and an identical transit rate must be used at each sampling vertical.

Figure 2 may be used as a guideline in selecting transit rates. The proper transit rate is one that gives a full bottle at the vertical having the greatest "unit width discharge." The maximum transit rate must not exceed 0.4 times the mean velocity, and the minimum rate must be sufficiently fast to keep from overfilling any of the sample bottles. Consequently, the transit rate to be used is limited by conditions (depth and velocity) at the sampling vertical containing the largest discharge per foot of width (largest product of depth times velocity).

A vertical transit rate not exceeding 40 percent of the stream velocity will satisfy all the limitations expressed for vertical transit rate (Guy and Norman, 1970). At this transit rate and with the axis of the sampler parallel to the flow, the resultant angle of approach of flow to the nozzle is about 20 degrees. According to the report (p. 32), the sampling error of concentration will be about 1 percent for 0.45-mm particles when the angle of approach is 20 degrees.

After selection of the sampling intervals, the vertical transit rate, the proper sampler, and proper nozzle size, sampling may be started from either bank. The sampler containing the sample bottle is lowered from the surface of the water to the streambed and immediately raised back to the surface, all at a constant rate and with the nozzle pointed directly into the flow. Care is needed not to disturb the streambed by bumping the sampler onto it or material dislodged from the bed may enter the nozzle, giving erroneous results. Each bottle is to be inspected and if coarse bed material is present, the bottle is emptied, rinsed, and resampled using the same sampling intervals or stations.

Several verticals may be sampled using the same bottle until the bottle is filled to within about 3 inches from the top. Do not fill the bottle more than this, as secondary circulation and enrichment of heavy particles may occur and the sediment concentration in the bottle will not be the same as the water-sediment mixture flowing in the stream. If overfilling does occur, the bottle is emptied, rinsed, and resampled using the same sampling intervals or stations.

When no more verticals can be safely sampled without overfilling the bottle, replace the full bottle with an empty one and continue sampling in the same manner until all verticals have been sampled. This procedure is the same whether sampling by wading methods or by reel and cable suspensions.

General guidelines for the EWI method of sampling are as follows:

1. Set out safety equipment where applicable (such as cones and signs) and assemble sampling equipment.

2. Locate the vertical containing the largest discharge per foot of width (largest product of the depth times velocity) by sounding for depth and estimating the velocity at several verticals near the center of flow.

3. If pint samples for suspended sediment and quart samples for chemical constituents are to be collected, determine the transit rates at the maximum discharge vertical for both the pint and quart containers.

   [ONCE DETERMINED, THIS TRANSIT RATE MUST
   BE USED FOR ALL OTHER VERTICALS]

4. From observations of depth, width, velocity, and sediment characteristics of the streamflow and a knowledge of the volume of sample required for analysis, determine the number of verticals to be sampled.

5. Determine the width of the segment to be sampled or the distance between verticals by dividing the stream width by the number of verticals decided upon. The stream width is determined from a tagline or from station markings on cableways and bridge railings. For example, if the stream width is 164 feet and the number of verticals is 10, the width of each segment to be sampled is 16.4 feet. For practical purposes, a vertical spacing of 16 feet is used. Thus, the location of the first vertical to be sampled would be at 8 feet. The second vertical would be located at 8 + 16 = 24 feet and so on (8, 24, 40, 56, 72, 88, 104, 120, 136, and 152 feet).

6. After determining the sampler transit rate and the number and locations of the verticals to be sampled, read and record the gage height and the time at which sampling is begun.

7. Move sampling and support equipment to first station to be sampled.

8. If concentrations of suspended sediment and chemical constituents are to be determined for the stream, collect separate samples for suspended sediment (in pint milk bottles) and chemical constituents (in quart bottles). A pint or quart bottle may be used to obtain samples from several verticals, provided the containers do not become completely filled. The individual suspended-sediment samples are not composited in the churn splitter by field personnel. The same quart glass bottle for chemical constituents is used for each vertical in the cross section. (Swirl the quart sample gently to keep sediment suspended and pour into churn after sampling each or several verticals.)

9. If either the pint or the quart container becomes completely filled during a sampling operation, discard the sample, as it will not be representative, and collect another sample.

[THE VOLUME OF THE SAMPLE WILL VARY CONSIDERABLY FROM
VERTICAL TO VERTICAL WHEN USING THE EWI METHOD]

If the depth and velocity vary greatly within the cross section, the volume of sample from some of the verticals will be very small. Thus, the total volume in the churn spitter, after all verticals have been sampled, may be insufficient for analytical requirements. If so, a second set of samples all at the same transit rate will be needed for all verticals. It must be remembered that complete sets of samples are to be collected--that is, sampling cannot be terminated until the far side of the stream is reached.

10. After sampling has been completed, label each of the pint sediment samples with the following information:

    a. Station number, name, and location of the stream.
    b. Date.
    c. Mean time and gage height (or discharge) for the period of sample collection (after step 12).
    d. Sampling location (location in vertical section).
    e. Water temperature.
    f. Initials of sample collector.

11. Read and record the gage height and time at which sample collection was completed.

12. Calculate and record on the field notes the mean time and gage height for the period of sample collection.

13. Complete field measurements, filtration, and preservation of samples as applicable.

14. Disassemble and clean samplers as described in the section "Methods of cleaning samplers and support equipment."

Other methods of surface-water sample collection

Because of Central Laboratory requirements for samples, and the possibility of contamination from the churn splitter and other circumstances, samples for some analyses may be collected by depth-integration samplers at a reduced number of verticals.

Organic constituents (to be analyzed by the Central Laboratory).--The possibility of contamination from the churn splitter precludes its use for compositing and splitting of samples for the analysis of organic constituents. All samples for analysis of organic constituents are to be collected in glass sample bottles. The Central Laboratory requires a 1-liter sample each for herbicides and insecticides. Both samples may be collected with a depth-integrating sampler with a nylon nozzle and silicone rubber gasket from a single vertical near the centroid of flow. If the depth and velocity permit the collection of a multivertical sample in the same bottle without overfilling (about 800 mL), the EDI method of sampling can be used with a minimum of three verticals. Samples for organic carbon are collected and transferred to a smaller container before shipment to the laboratory or processing in the field. Water from the collection container is agitated vigorously and immediately poured into the smaller container.

Surface and dip sampling

Sometimes a surface or dip sample will be satisfactory, especially when (1) stream velocity is too fast for the sampler to integrate, (2) large floating and moving submerged debris is present, or (3) stream depth is very shallow.

At some locations, stream velocities are so great that even 100-pound samplers will not reach the bottom. Under such circumstances, all except the largest of sediment particles will usually be thoroughly mixed with the flow, and a surface or dip sample collected with either a depth-integrating or a weighted-bottle sampler will be fairly representative.

In very shallow water where a depth-integrating sampler cannot be submerged, a representative sample usually can be obtained by immersing a hand-held bottle in the centroid of flow with the mouth of the bottle directed toward the current. Care should be taken to avoid getting the mouth of the bottle too close to the streambed and thereby collecting particles directly from the bed.

The quality of surface and dip samples is likely to be inferior to those obtained with depth-integrating samplers. As a result, these samples always need to be identified appropriately on the field notes.

Bed-material sampling

Data on the size of material comprising the streambed are useful for study of long-range changes in channel conditions and for use in computations of unmeasured or total load. Other programs, such as studies concerning the transport of pesticides, require collection and analysis of samples of the bed material.

The discussion of all the factors involved and some of the methods of collecting bed-material samples is beyond the scope of this manual. The methods utilized routinely for the collection of material finer than medium gravel for particle-size determination and pesticide analysis are described in the following sections. For a more comprehensive discussion of bed-material sampling, personnel are referred to the report, "Field Methods for Measurement of Fluvial Sediment" (Guy and Norman, 1970).

Material for particle-size analysis.--The BM-54 is the sampler commonly used for bed sampling in larger streams. The sampler weighs 100 pounds and is operated with a reel and crane from a bridge or from a cableway. To use the BM-54:

1. Set up the bridge crane or base or attach the sampler to the cable and reel for cableway operation.

2. Suspend the entire weight of the sampler by the hanger rod.

3. Cock the bucket in the open position with the allen wrench provided, being extremely careful to keep hands away from the bucket opening at all times.

4. With the reel, lower the sampler to the surface of the streambed. Avoid any jerking motions while lowering the sampler that would cause the cable to slaken and allow the bucket to close prematurely.

5. After the cocked sampler touches the streambed and tension is released on the line, lift the sampler slowly from the bed so the bucket will scoop a sample.

6. To remove the sample from the bucket, position the sampler above the sampler container and open the bucket with an allen wrench.

7. Label each sample container with the following information:

   a. Station number and name
   b. Date
   c. Mean time for the period of sampling
   d. Sampling location on bridge, tagline, or other
   e. Depth of water at vertical sampled
   f. Water temperature
   g. Initials of sample collector

8. Disassemble and clean sampler as described in the section "Methods of cleaning samplers and support equipment."

Material for pesticide analysis.--Samples of bed material for pesticides analysis by the Central Laboratory may be collected from a single vertical with the BM-54 sampler and placed in appropriate wide-mouth quart glass bottle. When depths are too shallow to use the BM-54 sampler, a sample can be scooped directly into the wide-mouth bottles. Bottom material at the selected vertical will ideally consist predominantly of sand, silt, and clay. Where possible, select a vertical that was also sampled for water-sediment mixture.

Label the sample container with the following information:

a. Station number, name, and location of the stream.
b. Date.
c. Mean time for period of the sampling.
d. Sampling location (location in vertical section).
e. Initials of sample collector.

Compositing and splitting of water-sediment samples

Sampling methods have been developed to produce samples that are representative of flow through a cross section. These methods frequently conclude with one bulk volume of water-sediment mixture. Unfortunately, preservation techniques and analytical methods do not always allow the submission of one sample in a single container to the laboratory for analysis. The sample must be subdivided, usually within a short time after collection, into a number of subsamples each of which must be virtually equivalent in concentration of suspended and dissolved constituents.

Churn splitter

The Geological Survey churn splitter is an apparatus available for splitting composite samples of water-sediment mixture into subsamples; its use is the only acceptable method of splitting samples containing sand-size material in the field. Samples may be taken from the churn splitter for analysis of all dissolved and suspended inorganic constituents. However, samples for the analysis of suspended sediment, pesticides, bacteria, TOC, SOC, DOC, DO, O&G, and radiochemicals cannot be taken from the churn. (See unpublished Quality of Water Branch Technical Memos Nos. 76-24T and 77.01). Two sizes of the churn splitter are available - the large size with a maximum volume of 14 liters and a small size of 8 liters.

The churn splitter allows obtaining different subsample volume for the sample while still maintaining the same basic chemical and physical properties of the original sample. The churn splitter has proven to be an invaluable tool for the collection and processing of composited cross-section samples from rivers and streams. The major disadvantages of the churn splitter are (1) sample volumes less than about 2 liters (4 liters for the 14-liter churn) cannot be split, and (2) inorganic sediments coarser than 62 micrometers cannot be split with an accuracy of less than about ± 10-15 percent.

The recent use of automatic samplers has introduced a problem that makes the use of the churn splitter impractical. Automatic samplers usually collect relatively fixed sample volumes, most of which are at or below the minimum volume of water required for proper operation of the smallest available churn splitter. Most automatic samplers collect only between 0.5 to 3 liters in one sampling cycle, which may not be enough volume for proper use of a churn splitter.

The laboratory may require several different subsamples for analysis. Samples collected by the EDI, EWI, or other methods are composited in either the 8-liter churn splitter or the 14-liter churn splitter and then are split into representative subsamples.

A total of 10 liters of subsamples of the water-sediment mixtures may be withdrawn from the 14-liter churn, whereas 5 liters may be withdrawn from the 8-liter churn. The 4 liters remaining in the 14-liter churn and the 3 liters remaining in the 8-liter churn are not used for water-sediment subsamples because the sediment distribution is not representative of the original sample. However, the water-sediment mixture remaining in either churn may be used for filtered subsamples for the determination of dissolved constituents.

The procedure for use of the churn splitter is as follows:

1. Clean churn as directed in section, "Methods of cleaning samplers and support equipment."

2. Before starting to collect samples to be composited in the churn, label all the subsample containers to be used and determine the total sample volume to be composited. Add to this sample volume at least 10 percent to cover filter losses and spillage.

3. Collect approximately 1 liter of water and thoroughly rinse the churn splitter.

4. Collect representative samples of the streamflow by using one of the methods described previously. Use only one sample bottle over and over again when collecting the samples to be composited, to minimize the amount of sediment lost in transferring from the bottle to the churn.

5. When the predetermined number of verticals in the cross section has been sampled and the required volume plus 10 percent for waste has been poured into the churn, place all water-sediment subsample containers within easy reach so that once started, the churning can be continuous.

6. Churn the sample at a uniform rate of about 9 inches per second. The disc needs to touch the bottom of the tank on every stroke and the stroke length needs to be as long as possible without breaking the water surface. If the churning rate is significantly greater than 9 inches per second or if the disc breaks the water surface, excessive air is introduced into the sample and may change the dissolved gases, bicarbonate, pH, and other characteristics of the sample. On the other hand, inadequate mixing may result in nonrepresentative subsamples.

7. After churning the sample in the splitter for about 10 strokes to assure uniform dispersion of the suspended material, begin the withdrawal of subsamples. As subsamples are withdrawn and the volume of sample in the churn decreases, maintain the churning rate of about 9 inches per second. If a break in withdrawals is necessary, the churning rate must be reestablished before withdrawals are continued.

8. After all the required water-sediment subsamples have been withdrawn, filter the sample remaining in the churn if the sample is to be analyzed for dissolved constituents.

9. After all filtered subsamples have been withdrawn, clean the mixing tank and churning disc thoroughly with deionized water. If water will not remove all the residue, clean as directed in section, "Methods of cleaning samplers and support equipment."

Cone splitter

The new cone splitter was first developed in December 1979 as a means to reliably subsample the samples collected for the Urban Hydrology Studies Program conducted by the U.S. Geological Survey in cooperation with the U.S. Environmental Protection Agency. Tests have shown that the cone splitter can split sample volumes as small as 250-mL into 10 equal subsamples, each subsample being within 3 percent of the correct volume and sediment concentration.

The cone splitter is a pour-through device. A funnel-shaped reservoir on the top receives the sample and directs it into the splitting chamber. Located in the reservoir funnel is a 2-mm-mesh screen, which retains large debris such as leaves that could clog or interfere with the splitting process. The screen reduces the vortex action of the water leaving the funnel and also helps mix the sample.

Below the funnel is a short section of stand pipe. Its function is to direct water as a steady stream into the splitting chamber, which contains a cone-shaped splitting head.

The cone splitter housing is machined from a solid block of Lucite or comparable material. Ten exit ports have been precisely drilled through one common point at a 45-degree angle from the vertical and spaced at 36-degree intervals around the circumference. The resultant configuration in the splitter chamber is a notched cone with 10 equally spaced exit ports about its base. There are no flat walls, benches, or surfaces inside the splitter chamber that can retain material or interfere with the splitting process.

The cone splitter works best when the following procedure is used. Practicing consistent procedure such as always tapping the assembly at the end of a split and always wetting the system before a split will help to assure unbiased results.

1. Set up the cone splitter on a flat open area. Check for level and proper tubing lengths. Visually inspect the splitter for broken parts, misalignment, or debris.

2. Rinse through 1 or 2 liters of deionized water. Discard the water.

3. Place containers under each outlet.

4. Shake the sample for 10 to 15 seconds.

5. Rapidly invert the sample container over the reservoir and rest it on the reservoir top.

6. After the flow has stopped, tap the assembly to dislodge adhering drops.

7. Remove desired subsamples. Repeat as necessary if any of the subsamples need splitting, starting with step 3.

8. At completion of all splits for the station being processed, disassemble the splitter and clean before splitting another sample.

All subsamples do not have to be collected in separate bottles. Outlet tubes can be combined to collect various combinations of the original sample. Care must be taken, however, when combining outlet tubes into a single bottle to make sure there is no backpressure resulting from restriction of the flow.

Consider for example, the following subsamples that are required from a 3-liter sample:

3 - 250 mL subsamples for chemical analyses (total recoverable).
1 - 500 mL subsample for chemical analysis (total recoverable).
2 - 250 mL subsamples for chemical analyses (dissolved).
1 - 500 mL subsample for chemical analysis (dissolved).

The sample then is split by placing a 500-mL bottle under each of three outlets, two outlet tubes are combined to a 1-liter bottle, and the remaining five outlet tubes can be combined into one convenient container for later filtering. The resulting split of the 3-liter sample would provide three 500-mL bottles having 300 mL each and one 1-liter bottle having 600 mL. There would then be 1,500 mL left for filtering.

If a more exact subsample volume is desired, the following procedure is used. For example, if 440 mL is required from a sample of 2,850 mL, the first step is to compute the percentage needed. In this instance, 450 mL is 16 percent of 2,850 mL. The 16-percent split is achieved by first obtaining 10 percent from one tube during the first pass. The remaining 6 percent is obtained by pouring one of the 10-percent splits through the splitter a second time and drawing off six tubes or 60 percent. By this procedure, a subsample of ± 1 percent of the whole sample can be obtained by two passes through the splitter.

Cone splitters must be cleaned before being used for processing any samples. Cleaning is not necessary before splitting repetitively from one sample, but between a series of samples from the same station and runoff event, rinse the splitter with several liters of distilled water. Before using a previously cleaned splitter, start by pouring several liters of deionized water through the splitter. After using a splitter, acquiring a new splitter, or before starting to process a sample from a different station, clean the splitter by disassembling it and washing the parts in soap and water using a good quality laboratory detergent. A soft bristle test-tube brush works well for cleaning inside the ports. Rinse thoroughly with tap water followed with deionized water. Store clean cone splitters in plastic bags between usages.

The cone splitters need to be visually inspected for damage, especially the cone splitting chamber. Retest units that show damage or wear to check their serviceability. Check discharge tubing frequently for proper length and cleanliness. Replace tubes as conditions warrant.

Sample filtration

Water-sediment samples that will be analyzed for the dissolved major inorganic and minor elements need to be filtered in the field. During some periods of flood runoff and rapidly changing stages for small urban streams, the necessity of collecting a large number of samples from several streams within a minimum period of time will preclude field filtration. Under these and other circumstances where field filtration is impractical, a sample filtered in the field service unit (laboratory) may be substituted with slightly less confidence in the reported data, provided that the raw sample is transported to the field service unit and filtered with a minimum of delay.

Samples for dissolved major inorganic constituents and trace metals

The equipment used for filtration of samples for the analysis of dissolved major inorganic and trace metals consists of a reversible, variable-speed battery-operated peristaltic pump, which forces the water-sediment sample through flexible silicone or tygon tubing into a 142-mm plate-type filter. There, the sediment is retained by a membrane filter while the filtrate passes through to a collecting vessel. Two plastic screens for use with the 142-mm plate provide support for the membrane filter (both above and below) and permit water flow in either direction without disruption of the membrane. Thus, when the membrane on the 142-mm plate becomes clogged with sediment during filtration, it can be backflushed to remove the sediment cake.

The following guidelines apply for filtration using the 142-mm backflushing filter:

1. Collect a composite water sample. This sample can be the water remaining in the churn after the raw samples have been drawn. The churn does not have to be agitated while drawing water that is to be filtered.

2. Open the plate filter. With forceps, place the bottom retainer screen on the base of the filter assembly. Next, one 0.45-micrometer pore-size filter membrane, 142-mm diameter, is placed on top of the bottom retainer screen. The top retainer screen is then placed in position. If no backflushing is anticipated, the top retainer screen can be omitted. For filtering water heavily laden with sediment, a prefilter can be added on top of the filter between it and the top screen. Do not interchange the bottom and top retainer screens. The bottom screen only contacts filtered water thereby avoiding any possible particulate contamination that may be present.

3. Close the filter by lightly tightening all bolts, followed by securely finger tightening opposite pairs.

4. Connect the pump discharge tube to the filter. Place the intake tube into the churn but not to the bottom to avoid drawing up the accumulation of settled material.

5. Check that power switch is off. Connect the pump to an appropriate power supply: AC, external DC, or internal rechargeable DC.

6. Turn pump on low speed and open air-vent valve located on top of plate filter. Tilt the filter slightly to allow all the trapped air to escape. Close the valve when the top is filled with water. Venting the trapped air is necessary because air will not pass through the filter membrane.

7. Flush the system by filtering 200 mL of sample. The flushing water can be collected and used as water to rinse sample bottles after wasting the first 50 mL. The flushing is necessary to equalize any ionic exchange capacity that may exist between the assembly and the water. A wetting agent is present in the filters to aid the initial transfer of water. Wasting the first 50 mL of water through the filter avoids most contamination from the wetting agent. Water heavily laden with sediment may clog the filter rapidly; therefore, it may be desirable to use distilled water to flush the filter assembly, followed by a minimum of 50 mL of stream water before collecting the filtrate samples.

8. Fill all necessary bottles with the filtrate. Securely cap any bottles not requiring further treatment. If rapid clogging of the filter is experienced before all needed water is collected, the filtering rate can be improved momentarily by backflushing.

9. To backflush the filter, place the discharge tube into a bottle of filtered water. Remove the intake tube from the supply water. Reverse the pump direction. Turn the pump on full speed drawing the filtered water back through the filter. Much of the sediment cake is washed loose and backflushed through the pump and out of the system. Normal filtering can be resumed after backflushing.

10. After each field use, cycle the filtration apparatus with distilled water, then disassemble and rinse all sections. Upon discarding the used filter membrane, the screens are not to come in contact with one another and are to remain in their original top and bottom position. During nonuse, a membrane filter or filter divider is to be placed between the screens. After cleaning, teflon hose ends are to be placed in separate plastic bags for protection. Generally, after field trips or on a periodic schedule, cleaning is done more thoroughly. After disassembly, all components are cleaned using a laboratory detergent. This cleaning can be followed by alternate baths of chlorox and a 5-percent solution of hydrochloric acid. A glass pie pan with 1/4-inch depth of cleaning solution can be used as a bath. In place of the acid bath the solution can be cycled through the assembled apparatus using the pump. Follow acid cleaning with several rinsings using distilled water.

Samples for dissolved (DOC) and suspended (SOC) organic carbon

The proper collection and filtration of water samples are essential to obtain accurate DOC (dissolved organic carbon) and SOC (suspended organic carbon) analyses and are critical for the correct interpretation of the data. A representative, depth-integrated stream sample may be taken at one or more vertical sections by filling a 1-liter clean glass bottle near the centroid of discharge. A sampler modified for organic use with teflon nozzle and gaskets probably is best. A representative ground-water sample may be collected by a modified thief sampler after the water standing in the casing has been removed.

A special filtration unit consisting of a small pressure cylinder of zero grade (carbon free) nitrogen gas, a pressure regulator, and a stainless steel filter assembly fitted with flexible silicone or tygon tubing and a 47-mm, 0.45-micrometer silver membrane filter is used for filtering DOC and SOC samples. (Do not use plastic membrane filters!)

Samples for DOC and SOC are filtered into 100-mL organically clean glass bottles supplied by the Central Laboratory.

[DO NOT USE SUBSAMPLES COMPOSITED IN THE GEOLOGICAL SURVEY CHURN SPLITTER]

Samples for DOC and SOC analyses are preserved by the combined effects of filtration, chilling, and contact with silver. Most organisms will not pass through a 0.45-micrometer filter. The sample bottle is also sterilized by heating at 550°C for 12 hours. Elemental silver is dissolved from the silver filter during filtration. Approximately 1 µg (microgram) of silver is dissolved per mL of water filtered. Silver in solution or as a colloid exhibits bacteriocidal properties. In addition to the filtering and bacteroid effects of silver, the samples are sealed in a water-tight container and kept chilled on ice until analysis.

The following guidelines apply for filtration:

Suspended Organic Carbon (SOC).--

1. Remove the filter assembly from the aluminum foil wrap and disassemble.

2. With a pair of stainless steel forceps, place a silver membrane filter on the filter assembly base between the support screen and the teflon seal ring.

3. Screw the base on the funnel barrel.

4. Pour about 50 mL of distilled water into the funnel barrel, screw on the top part of the filter assembly barrel, and attach to the pressure tank.

5. Turn the handle on the pressure regulator counter-clockwise for several turns until the pressure regulator valve is closed. Open the valve to the nitrogen cylinder. Open the valve to the pressure regulator by turning the handle clockwise until 12-15 pounds of pressure registers on the gage.

[EACH UNIT NEEDS TO BE EQUIPPED WITH A POP-OFF VALVE SET AT 20 POUNDS OF PRESSURE]

6. Filter and discard the filtrate from the distilled water rinse.

7. Close the valve to the nitrogen cylinder. After the pressure gage shows no pressure, close the valve to the pressure regulator.

8. Remove the top cap of the filter assembly. Shake the sample for SOC vigorously to resuspend the settled particles and immediately transfer (by clean pipet or graduated cylinder) the required volume of sample to the filter funnel barrel. Repeat step 5 and filter the required volume of sample.

The volume of water to be filtered for SOC analysis depends upon the concentration of suspended sediment in the water-sediment sample. The following volumes will provide good results:

Approximate suspended-sediment concentration, in milligrams per liter	Volume of water-sediment sample to be filtered, in milliliters
0 - 100	100
100 - 500	50
500 - 1,000	25
More than 1,000	10

The usual method for processing suspended and dissolved organic carbon compounds is to filter the sample through a silver filter, reserve the filtrate for DOC analysis and the silver filter for SOC. However, when sediment concentrations get to be more than about 1,000 mg/L (milligrams per liter), it is difficult, if not impossible, to pass the required 30 to 50 mL through the filter for the DOC analysis. The following method can be used when the suspended-sediment concentration exceeds 1,000 mg/L.

a. Collect sample in a container not made of carbon compounds and that has been well rinsed in native water.

b. Let sample settle for about half a day, or long enough so that most of the sediment has settled out (don't refrigerate).

c. Filter the supernatant through the silver filter. Collect at least 30 mL, but preferably 50 mL (it takes at least 15 mL to conduct a DOC analysis, and the laboratory conducts two analyses on each sample).

d. Pour off the extra water from the settled sample.

   e. Ship the filtered sample (iced) and the unfiltered mud (not iced). Be sure to label the bottle containing the settled portion of the sample as to how much water was originally collected.

   f. Discard the filters.

9. After completing the filtration, depressurize the filtration apparatus (step 7) and disassemble. With a pair of stainless steel forceps, remove the silver membrane, fold the membrane in half with the filter cake on the inside, and place the folded filter in a petri dish.

10. Place a gummed label on the outside of the petri-dish cover, identify the sample, record the volume filtered, and insert the petri dish in a whirl-pack bag. Chill the sample in the petri dish immediately on crushed ice in an ice chest.

Dissolved Organic Carbon (DOC).--

1. Send a minimum of about 80 mL of sample to the laboratory for the analysis of DOC. If this volume can be obtained by collecting the sample filtrate from the SOC sample, it can be used for the analysis of DOC. Otherwise the following steps are needed.

2. With a pair of stainless steel forceps, place a new silver filter on the filter base between the support screen and the teflon seal ring.

3. Screw the base on the funnel barrel.

4. If a sample for SOC has been prepared, no additional rinsing of the filter assembly is required. If a sample for SOC has not been filtered, rinse assembly with distilled water as described in step 4 of the procedure for SOC.

5. Transfer about 100 mL of the water-sediment sample to the filter funnel barrel, screw on the top part of the filter assembly barrel, and attach to the pressure tank. Place the discharge tube into the receiving vessel.

6. Pressurize the filtration apparatus as described in step 5 of the procedure for SOC. (Discard first 10 to 15 mL of filtrate if an SOC sample has not been filtered.)

7. Continue the filtration process until a 100-mL sample is filtered and collect the filtrate in the appropriately labeled 100-mL DOC bottle. Place the sample bottle on crushed ice.

8. After completing the filtration, depressurize the filtration apparatus and disassemble.

9. Rinse the filter assembly several times with small volumes of distilled water and place in clean aluminum foil wrap for storage.

SELECTION AND MAINTENANCE OF FIELD INSTRUMENTS

Before departing on a field trip, check the operation and calibration of all field instruments to ensure that they are in good working condition. Temperature compensators need to be checked for several temperature ranges. If field meters cannot be calibrated against standard solutions with known values or if readings are sluggish or erratic, try to isolate the problem between the probe or meter. If a spare probe is available, change the probe. If this solves the problem, inspect the defective probe and consider the possibility of repair. The pH probe, for example, may be scratched or broken, the filling solution may be low or contaminated, or the lead may be broken. The membrane on the dissolved-oxygen probe may be torn, the filling solution may be contaminated or may contain an air bubble, or the lead may be broken. The conductivity cell may be dirty, the platinum or silver may have flaked off, or the lead may be broken. If these or similar problems arise, try remedial procedures suggested by the manufacturer.

If the problem is with the instrument rather than the probe, contact the District Equipment and Supply Coordinator. The instrument can be exchanged for another unit. If the problem instrument cannot be repaired within the District, a decision based on cost will be made as to how or if repair can be done.

Water-quality parameters commonly measured in the field are water temperature, specific conductance, pH, alkalinity, carbonate, bicarbonate, dissolved oxygen (DO), and indicator bacteria. Field water-quality instruments, support equipment, and some of the reagents used for the measurement of these parameters are listed in the following tabulation. For a more thorough discussion of the reagents, see section entitled "Reagents for field determinations" and the report "Methods for Determination of Inorganic Substances in Water and Fluvial Sediments" (Skougstad and others, 1979).

Water temperature

1. Thermometer capable of measuring temperatures ranging from -5° to 45°C.

2. Meters with resistance-type thermistors.

    a. Ocean Data Equipment (ODEC) Meter
    b. YSI Model 54 DO Meter with appropriate probes.
    c. Martek, Model Mark 6
    d. Envirolab continuous monitor
    e. USGS Mini Monitor

Specific conductance

1. Conductivity meters.

    a. Lab line and Electronic Switch Gear, Model Mark IV, with cup-type probes
    b. YSI, Model 32 with appropriate cells
    c. ODEC multiparameter instrument
    d. USGS minimonitor with probe type cell
    e. Martek, Model Mark 6, with probe

2. Conductivity standards.

    a. Standards obtained from Central Laboratory, as applicable.

pH

1. pH meters.

    a. Sargent Welch, Model PBL
    b. Extech, Model 609.
    c. Aqua Monitor, Model 8000.
    d. Martek, Model Mark 6, with probe

2. pH buffers.

    a. pH 4 buffer.
    b. pH 7 buffer.
    c. pH 10 buffer.

3. Glassware.

4. Electrode filling solution.

5. Kimwipes or equivalent.

Alkalinity, carbonate, and bicarbonate

1. pH meter, with appropriate electrode.

    a. Portable magnetic stirrer with stirring bars, stirring rods, or other mechanical stirring devices.
    b. Graduated cylinder.
    c. Buret (25 mL) with stand or digital titrator.
    d. 0.01639 N sulfuric acid (or other given normality).
    e. 100-mL beakers.

Dissolved oxygen (DO)

1. YSI Model 54 or Martek or ODEC Oxygen Meter or equivalent, with appropriate probe.

    a. Membrane repair kit with electrolyte and membranes.
    b. Portable magnetic stirrer with stirring bars.
    c. BOD bottle.
    d. Barometer.
    e. Calibration chamber, YSI model 5075 or equivalent.

2. Chemicals and equipment for "Modified Winkler Method."

    a. Solutions of potassium fluoride, manganous sulfate, alkali-iodide-azide, sulfuric acid, and 0.025 N phenylarsine oxide.

   b. 10-mL buret.
   c. magnetic stirrer and stirring bar.
   d. glassware including BOD sample bottle, 102-mL measuring flask, widemouth erlenmeyer flask.

Bacteria

1. Filter-holder assembly, Millipore (XX6300120) or equivalent, with vacuum pump and two-way valve.

   a. Membrane filters, white, grid, sterile packed, 0.7 micrometer pore size, 47-mm diameter.
   b. Plastic petri dishes with cover, disposable.
   c. Forceps, stainless steel, smooth tip.
   d. Milk dilution bottles.
   e. Pipets of 1.0 and 10 mL capacity.
   f. Sterile graduated cylinders, 100 mL capacity.
   g. Vacuum bulb for pipeting.
   h. Methyl alcohol, for sterilizing filter holder assembly and forceps.
   i. Alcohol burner or candle.
   j. M-Endo agar medium kits for total coliform bacteria.
   k. M-FC agar medium kits for fecal coliform bacteria.
   l. KF streptococcus agar medium kits for fecal streptococcal bacteria.
   m. Sterile buffered dilution water.
   n. Microscope or other magnification source (X10 to X15 magnification).

2. Portable Heaterblock incubator, Millipore or equivalent.

3. Autoclave

FIELD-MEASUREMENT METHODS

Water temperature

The effect of water temperature on density and gas solubility is of primary concern. Density plays a major role in mixing of different water masses, especially where seasonal stratification occurs, and the solubilities of dissolved gases are inversely proportional to the temperature of the water. Temperature also affects the rate of chemical reactions, biological activity, conductivity, and pH.

The thermometer is the most widely used device for temperature measurements. It consists of a thin-walled glass bulb joined to a glass capillary stem closed at the opposite end. The bulb and part of the stem are filled with an expansive fluid, either mercury or alcohol. The fluid in the bulb expands or contracts in volume as its temperature rises or falls. The volume change is transmitted to the capillary tube, causing a change in the liquid column length. Graduations on the stem denote change in column length as a function of temperature.

A thermistor is an electrical device made of a solid semiconductor with a large temperature coefficient of resistivity, which would exhibit a linear voltage characteristic if its temperature were held constant. It changes electrical resistance markedly with temperature change, the relationship usually being exponential.

An electric signal processor converts the resistance changes to a readout calibrated in temperature units.

Thermistors can be constructed with extreme sensitivity but are subject to a variety of errors. Therefore, they need to be calibrated frequently at many points to assure reasonable accuracy.

Field measurements of temperature include both an air-temperature reading and a water-temperature reading. Air-temperature readings are made by using a dry thermometer placed in a shaded area protected from strong winds but open to adequate air circulation. Avoid areas that may have radiant heat effects such as near metal walls or sides of vehicles. Allow the thermometer to equilibrate for a minimum of 10 minutes before recording the temperature. Record the temperature to the nearest 0.5°C and the time of day of the measurement.

Water temperatures are made in such a manner as to represent the mean temperature of the stream at the time of observation. To do this, a cross-section profile is first made to determine the variability, if any, that exists. A thermistor-type unit works best for this purpose because it allows, in addition to numerous cross-section observations, several observations in the vertical. For streams having a fairly uniform velocity profile, equal distant temperature measurements (5 to 10 measurements) can be made and averaged to report the mean stream water temperature to 0.5°C. Temperatures of streams with greatly variable velocity profiles are computed on a flow rated observation scheme. This can be simply conducted by dividing the cross-sectional area into areas of equal discharge. Five sections are sufficient for most streams. Measure the temperature in the center of each section and average the results.

For streams that have a fairly uniform temperature (less than 2°C variance for 95 percent of the time), one measurement can be made and reported as the stream temperature. To make this measurement, suspend, place, or hold a thermometer or thermistor in the main flow of the stream. If possible, try to keep the thermometer in a shadow area to prevent erroneous readings caused by direct solar radiation. The thermometer needs to be immersed in the stream for a minimum of 1 minute prior to making measurements. The thermometer is read while the bulb is submerged. Thermistor probes are immersed for a minimum of 3 minutes if the thermistor is an integral part of a combination probe such as is true for the dissolved oxygen probe. Immersion is necessary to allow the temperature of the mass of the probe to come to equilibrium with the water.

Measurements from overhead structures are best made by using a thermistor. If a thermometer is used, it is mounted in a holder that will allow a sample of water to be retrieved in order to keep the thermometer submerged while reading. The thermometer assembly is suspended in the stream for 3 to 5 minutes prior to retrieval. When retrieved for a reading, keep the container upright and do not delay in reading the temperature.

If the stream is too deep to be waded, or if the water is too rough, swift, or turbid to allow an in situ measurement, the temperature can be measured by collecting a sample with a tubular insert sampler or BOD sampler, immediately immersing the thermometer in the container, and reading the thermometer. The container must be large enough to allow full immersion of the thermometer, and the sample container must be brought to the same temperature as the stream. In addition, the container must provide sufficient mass to ensure that the temperature of the water does not change while it is being measured.

Calibration and calibration checks

New thermometers (and thermistors) when received from the manufacturer will be checked in a constant temperature water bath at two temperatures (approximately at 0° and 20°C) using an ASTM certified thermometer or equivalent. Field grade thermometers must agree within 0.5°C and laboratory grade thermometers must agree within 0.2°C. Thermometers that are not acceptable are discarded or returned to the manufacturer. Thermistors are calibrated to bath temperatures.

To check calibration of thermometers follow the general procedure outlined below:

1. Freeze several ice cube trays of distilled water.

2. Fill a 500-mL glass beaker three-fourths full with the cracked ice. Add chilled distilled water to the beaker. Place the beaker of ice and water in a larger container that has been filled with crushed ice. Place a thermometer certified by ASTM (American Society for Testing and Materials) in the ice/water mixture and observe that the temperature is uniform at or near 0.0°C.

3. Check the calibration by adding to the ice/water mixture several field thermometers that have first been pre-chilled to 0°C by storing in a separate ice/water bath.

4. Wait 2 minutes before making temperature measurements. Periodically stir the ice/water mixture and check the temperature. With the thermometers still submerged to the maximum amount still allowing readings to be made, compare the temperature of the ASTM-certified thermometer and each field thermometer. If found to be within ± 0.5°C of the ASTM-certified thermometer, then set aside for calibration checking at a higher temperature. Thermometers with differences greater than ± 0.5°C are to be discarded or returned to the manufacturer for replacement.

5. For room temperature (about 20°C) calibration check, place a container (about 1 gallon of water) in a box filled with packing insulation. Place the calibration chamber in an area of the room with a fairly constant temperature (areas away from drafts, vents, windows, and harsh lights).

6. Immerse the ASTM-certified thermometers and field thermometers in the water, cover, and let sit overnight.

7. Check for uniform temperature in a container with a calibration thermometer, then compare the ASTM-certified thermometer with each field thermometer.

8. Thermometers found acceptable for field use can be marked with a red ring (fingernail polish). Discard or return unacceptable thermometers to the manufacturer.

Thermistor temperature recorders can be calibrated in the same manner described above, but with the additional steps of making intermediate and higher temperature checks. These checks are made by placing a large beaker of ice water on a magnetic stirrer and with slow stirring, allow the container to slowly come to room temperature. Throughout the whole period, periodically read the ASTM-certified thermometer and thermistor readings. Keep both the ASTM-certified thermometer and the thermistor probe in the container at all times. Periodically check the batteries of the meter unit for proper setting.

Field and laboratory grade thermometers are assigned to field personnel as required and checked on a biannual schedule or for project work at the beginning of the field season. Each support laboratory assigns an individual for the checking and record keeping. Thermometers meeting the criteria listed above for new thermometers will be tagged with the date and certified for use. All thermometers in use (including backup thermometers) need to have a tagged date younger than 6 months. The responsibility to see that biannual checks are made lies with personnel using the thermometers.

In situ probes for permanent temperature recorders are checked, and recalibrated if necessary, on a periodic schedule. Laboratory grade thermometers are used for this purpose and calibration is to the nearest 0.1°C. The temperature is measured with a thermometer as near to the probe as possible. On no less than a seasonal basis, a cross sectional survey of stream temperature is to be made and documented to show that the temperature measured by the probe represents the average temperature of the stream cross section. If the survey shows otherwise, then the probe may need to be relocated.

Reporting

Report all routine observation temperature measurements to the nearest 0.5°C. For special studies where greater or less precision is requested, report temperatures to the requested precision.

Specific conductance

Specific conductance is a measure of the ability of water to conduct an electric current and is an indication of the ionic strength of the solution. Specific conductance is the reciprocal of specific resistance in ohms and is reported in microsiemens per centimeter at 25°C (formerly reported in micromhos per centimeter at 25°C; the conversion is 1:1). The determination is easily made, and the results are useful as general indications of dissolved-solids concentrations.

The specific conductance of some waters may change significantly with time because of such chemical and physical reactions as precipitation, adsorption, ion exchange, oxidation, and reduction. Therefore, specific conductance is measured in the field, where possible, with an accurate conductivity meter. Occasionally, the error in field measurements is great, and care is needed to prevent errors in temperature measurements or compensation, rapid changes of the water temperature when specific conductance is being measured, entrapment of air in the conductivity cell, a dirty conductivity cell, an improper cell for range of conductivity, or a large concentration of suspended sediment in the sample.

The following description is for the Model Mark IV conductivity meter.

Cleaning the cells

The measuring cell requires cleaning on a periodic basis and specifically if standard solutions show the instrument to be in error. If the cell is not cleaned periodically, deposition of salts can occur, which will cause inaccurate readings.

1. Remove the plastic bung from the bottom of the cell, where applicable.
2. Using the bottle brush provided, scrub the bore of the cell with a 50-percent water/detergent solution and rinse thoroughly with distilled water. Shake out the surplus water and examine the cell to ensure that the electrodes and interior surfaces are evenly wetted (that is, that there are no grease deposits); if the surfaces are not evenly wetted, repeat the procedure and replace the plastic bung.
3. A 1-percent hydrochloric acid solution may be used for more stubborn deposits. Wash cell thoroughly with distilled water after treatment with hydrochloric acid.

Test procedure

The calibration of the instrument and the battery condition can be easily and quickly checked by the following steps:

1. Set the function switch to the TEST position and depress the HOLD ON button.
2. Rotate the large calibration dial until the null balance indicator pointer coincides with the cursor line above it; the dial reading opposite the cursor should be at the 1.0 mark. If the dial reading is not at the 1.0 mark, readjust the instrument dial (see section Field-measurement methods, Specific conductance, Calibration check).
3. To check the battery condition, set the function switch to any one of the three measuring ranges, and depress the HOLD ON button; the null balance indicator pointer should show full scale deflection. If it does not, replace the battery.

Making the measurement

Connect the selected measuring cell to the coaxial socket labeled MEASURING, using the length of coaxial cable provided. It is not significant which wires are connected to which terminal on the cell, as they can be connected either way.

For the most precise accuracy throughout the measuring range, the beaker cell with a constant 0.1 is used for measurement between 0.1 and 1,000 microsiemens. The cell with a constant of 1.0 is used from 100 microsiemens and above. Overlap occurs where both cells function equally well. If the order of conductivity of the sample is not known, first select the 0.1 constant cell.

To measure conductivity, proceed as follows:

1. Fill the selected measuring cell with the sample to be measured and plug its connecting cable into the MEASURING socket.

2. Measure the temperature of the sample using the mercury thermometer provided.

3. Set the TEMP °C knob to the value measured by the thermometer, and remove the thermometer from the cell.

4. Set the function switch to the anticipated range of measurement.

5. Depress the HOLD ON button and slowly rotate the graduated dial until the edgewise balance indicator shows center scale precisely. Read off the dial setting at which this occurs and multiply by the range factor for the appropriate function switch position and cell constant. If balance has been obtained with the function switch in the second range position, the reading obtained is the electrolytic conductivity at the standard temperature of 25°C. If balance has been obtained with the function switch in the first or third range positions, the reading obtained is the electrolytic conductivity at the temperature measured by the thermometer.

The temperature compensation provided on the second range (10^3, using 1.0 cell constant) position by the TEMP °C control applies correction on the basis of a temperature coefficient of conductivity of 2 percent per °C, which is only substantially true for weak aqueous solutions in the range 10 to 10,000 microsiemens. Outside this range, or for greater accuracy within it, a modified procedure is adopted:

1. Set the TEMP °C knob to the 25°C setting, and warm the sample so that it is a few degrees in excess of 25°C.

2. Pour the sample into the measuring cell and note its temperature with the mercury thermometer.

3. When it has cooled to 25°C, immediately remove the thermometer and make the measurement.

To make specific-conductance measurements on the two outer scale settings, first allow the temperature of the sample to approach as close a possible to 25°C. Do not delay more than 2 hours. Record temperature and measure conductivity as previously described. Correct the conductivity observed to specific conductance at 25°C by the following equation:

$$SC_{25} = C_t F_t \qquad (1)$$

where SC_{25} = specific conductance at 25°C.
C_t = conductivity measured at temperature t.
F_t = correction factor at temperature t.

The correction factor (F_t) is computed from the parabolic curve equation:

$$F_t = A_0 + A_1 t + A_2 t^2 \qquad (2)$$

where (for potassium base water) $A_0 = 1.8900$
$A_1 = -0.05559$
$A_2 = 0.00081$

and the temperature is between 1° and 25°C.

A new equation can be computed for the water type being measured by measuring the conductivity (C_t) at various temperatures and at 25°C (SC_{25}). The F_t is computed by:

$$F_t = \frac{SC_{25^\circ}}{C_t} \quad (3)$$

The derived F_t values are used in a least-squares curve fit to obtain the new parabolic equation constants A_0, A_1, and A_2.

Using the potassium-based constants on nonpotassium-based waters introduces insignificant errors for the general purpose meters used in measuring conductivity. For most general purpose measurements, table 1 can be used.

Table 1.--*Correction factors for converting non-temperature compensated conductivity values to specific conductance at 25°C, based on a 1,000 microsiemens KCl solution*

[°C, degrees Celsius]

Temperature (°C)	Factor	Temperature (°C)	Factor	Temperature (°C)	Factor
0.5	1.87	10.5	1.39	20.5	1.09
1.0	1.84	11.0	1.37	21.0	1.08
1.5	1.81	11.5	1.35	21.5	1.07
2.0	1.78	12.0	1.33	22.0	1.06
2.5	1.76	12.5	1.32	22.5	1.05
3.0	1.73	13.0	1.30	23.0	1.04
3.5	1.70	13.5	1.28	23.5	1.03
4.0	1.68	14.0	1.27	24.0	1.02
4.5	1.66	14.5	1.26	24.5	1.01
5.0	1.63	15.0	1.24	25.0	1.00
5.5	1.60	15.5	1.22	25.5	.99
6.0	1.58	16.0	1.21	26.0	.98
6.5	1.56	16.5	1.19	26.5	.97
7.0	1.54	17.0	1.18	27.0	.96
7.5	1.52	17.5	1.16	27.5	.95
8.0	1.49	18.0	1.15	28.0	.94
8.5	1.47	18.5	1.14	28.5	.93
9.0	1.45	19.0	1.13	29.0	.92
9.5	1.43	19.5	1.12	29.5	.91
10.0	1.41	20.0	1.11	30.0	.90

Comparison of two solutions

By using two measuring cells--one connected to the MEASURING socket, the other to the COMPARISON socket--the Mark IV may be used to make direct comparisons of the conductivities of two samples. Fill two identical measuring cells with the solutions to be compared and connect the cells to the COMPARISON and MEASURING sockets. Turn range selector to "compare," hold "press button" down and rotate measuring dial until balance is indicated. The conductivity ratio may then be read directly from dial.

The particular end of the scale at which balance occurs determines which of the two cells contains the sample of greater conductivity, because the ratio measured is always MEASURING : COMPARISON. Thus, for example, a balance at the 10 mark on the dial denotes that the sample conductivity in the MEASURING cell is 10 times that of the COMPARISON cell, whereas a balance at the 0.1 mark denotes the exact reverse.

Determination of cell constant

When the constant of the conductivity cell is unknown, or known only approximately, it can be determined by the use of a solution of known specific conductance. A 0.00702 N potassium chloride (KCl) solution has a specific conductance of 1,000 microsiemens per centimeter at 25°C. The following table indicates that the conductance of this solution changes about 2 percent per Celsius degree near 25°C.

Temperature (°C)	Conductance (microsiemens)	Temperature (°C)	Conductance (microsiemens)
18.0	860	24.5	990
18.5	870	25.0	1,000
19.0	880	25.5	1,010
19.5	890	26.0	1,020
20.0	900	26.5	1,030
20.5	910	27.0	1,040
21.0	920	27.5	1,050
21.5	930	28.0	1,060
22.0	940	28.5	1,070
22.5	950	29.0	1,080
23.0	960	29.5	1,090
23.5	970	30.0	1,100
24.0	980		

The relationship of the cell constant to the theoretical specific conductance of a standard solution at a given temperature and to the observed specific conductance of the standard solution at the same temperature is shown by the following equation:

$$\text{Cell constant} = \frac{\text{theoretical specific conductance at given temperature}}{\text{observed specific conductance at same temperature}} \qquad (4)$$

Thus, if the cell were filled with a 0.00702 N KCl solution at 25°C and the observed conductance (meter reading x conductivity multiplier) were 909 microsiemens, the constant would be:

$$\text{Cell constant} = \frac{1{,}000 \text{ microsiemens}}{909} = 1.10 \qquad (5)$$

Calibration check

Specific conductance standards are available from the Denver Central Laboratory. Each field service unit responsible for measuring specific conductance can obtain appropriate standards from the laboratory.

Prior to each field trip or when measuring multiple samples, standards need to be measured that will bracket the expe[illegible] In addition, on a daily basis or more frequently if sample variability exists, a standard needs to be measured that falls near the expected value of the sample(s). These calibration checks are to be entered into the permanent meter book or on field note forms.

1. If observed readings are low, soak cell in a warm detergent solution, rinse with tap water and deionized water, and repeat readings. If the observed readings are consistently more than about 3 percent less than theoretical values of freshly prepared standards, the electrode may require replatinization or the cell constant may be erroneous.

2. If observed readings are consistently more than 3 percent greater than theoretical values, the cell constant needs rechecking.

3. If the conductivity meter has an inherent error that cannot be corrected by changing cells, calibration curves can be prepared. Additionally, if this error is present when the selector knob is on the temperature compensating scale (second position), calibration can be done as follows:

    a. Select three standards that fall near the two extremes and midrange of all expected sample measurements.

    b. Place the selector in TEST position and check to see that the needle is at center scale when dial is at 1.0. Loosen dial and readjust if necessary. If meter continues to be off calibration when checked against standards, proceed with steps c-f.

    c. Remove knob from temperature control.

    d. Pour midrange standard into cup and measure temperature accurately. Place dial exactly on reading given for standard.

    e. Turn temperature control (with knob removed) until dial needle centers without moving dial. Carefully replace and tighten temperature knob so that pointer is on the exact measured temperature of the standard.

    f. Make calibration checks of the two standards representing the extreme range. If small errors exist it may be possible to split the differences using the above method.

Reporting the results

Conductivity measurements are reported as specific conductance in microsiemens per centimeter at 25°C. Results are reported to three significant figures, whole numbers only. Exceptions to this rule may be in special programs, such as in measuring atmospheric water, where values are commonly expressed as whole numbers and one decimal place.

pH

The pH of a solution is a measure of the effective hydrogen-ion concentration (activity). In aqueous solutions, pH is controlled primarily by the hydrolysis of salts of strong bases and weak acids or vice versa. According to Hem (1970) the activity of hydrogen ions can be most conveniently expressed in logarithmic units, and the abbreviation "pH" is now generally taken to mean a measure of the hydrogen-ion activity $[H^+]$. At pH 7, 1×10^{-7} moles per liter of the hydrogen ion is present, and the hydrogen-ion content does not begin to approach the status of a major component of the solution until the pH is below 4.0. Dissolved gases such as carbon dioxide, hydrogen sulfide, and ammonia also affect the pH appreciably. Degasification (such as loss of carbon dioxide), precipitation (such as calcium carbonate), and other chemical and physical reactions may cause the pH of a water sample to change significantly within several hours or even minutes after the sample is collected. Immediate analysis of a sample in the field is required if dependable results are to be obtained.

A more thorough discussion of pH is included in the report "Guidelines for Collection and Field Analysis of Ground-Water Samples for Selected Unstable Constituents" (Wood, 1976) and "Methods for Determination of Inorganic Substances in Water and Fluvial Sediments" (Skougstad and others, 1979). Instruments commonly used for field measurement of pH are the Sargent Welch Model PBL, Extech Model 609, Aqua Monitor Model 8000, and the Martek Model Mark 6.

The following section provides guidelines for pH measurements with the Sargent Welch Model PBL Portable pH Meter. For operating instructions for other field pH meters, refer to instruction manuals provided by the manufacturer.

Calibration check

After the meter has had sufficient time to warm up, it must be calibrated using two or more buffers prior to making the pH measurements. To calibrate the meter follow the procedure as listed:

1. Buffers used in calibration need to be at approximately the same temperature as the sample. In the field it may be necessary to place the sealed bottles of buffers in the stream for a period sufficient for them to come within 5°C of the stream temperature.

2. In the meter OFF position, check to determine if the meter pointer rests exactly on 7.0. If not, reposition pointer using screw adjustment on meter face.

3. Plug electrode into meter and turn meter to STANDBY position. Slide down sleeve covering the filling hole at the top of the electrode and remove solution holding cap at the bottom of electrode. Rinse electrode with deionized water and gently blot dry with soft absorbent tissue.

4. Measure temperature of buffer 7 solution and set TEMPERATURE dial to this reading. Immerse the electrode in buffer 7 solution and from tables 2-4, showing temperature versus pH of the buffer, determine the theoretical value of the buffer.

5. Turn the meter from STANDBY to READ and using STANDARDIZATION control adjust pointer until it rests exactly on the table value for pH 7 obtained in step 4. Turn meter to STANDBY, remove probe, and rinse thoroughly with distilled water followed by gentle blotting with soft absorbent tissue.

6. Measure temperature of buffer 10 solution and set TEMPERATURE dial to this reading. Immerse the elecrode in the buffer 10 solution and from tables 2-4 determine the theoretical value of the buffer.

Table 2.--*Effects of temperature on Beckman buffers*

[°C, degrees Celsius]

Temperature (°C)	pH (units)	Temperature (°C)	pH (units)	Temperature (°C)	pH (units)
Beckman phthalate pH 4 buffer (Color code--Red)					
0	4.00	30	4.02	70	4.13
10	4.00	40	4.04	80	4.16
20	4.00	50	4.06	90	4.21
25	4.01	60	4.09	95	4.23
Beckman phosphate pH 7 buffer (Color code--Green)					
0	7.10	30	6.99	70	6.99
10	7.06	40	6.98	80	7.00
20	7.02	50	6.97	90	7.02
25	7.00	60	6.98	95	7.03
Beckman carbonate pH 10 buffer (Color code--Blue)					
0	10.32	20	10.06	40	9.89
5	10.25	25	10.01	45	9.86
10	10.18	30	9.97	50	9.83
15	10.12	35	9.93		

Table 3.--*Effects of temperature on Hydrion buffers, Scientific Products Catalog No. H7602*

[°C, degrees Celsius]

Temperature (°C)	pH buffer							
	2.00	4.00	5.00	6.86	7.00	9.00	10.00	12.00
5	1.85	3.99	5.07	6.95	7.08	9.21	10.22	12.56
10	1.89	3.99	5.04	6.92	7.06	9.15	10.16	12.35
20	1.96	3.99	5.01	6.88	7.01	9.05	10.05	12.14
25	2.00	4.00	5.00	6.86	7.00	9.00	10.00	12.00
30	2.03	4.01	4.99	6.85	6.99	8.96	9.95	11.89
40	2.08	4.03	4.98	6.84	6.98	8.89	9.88	11.71
50	2.12	4.05	4.97	6.83	6.97	8.83	9.84	11.52
60	2.14	4.08	4.98	6.84	6.98	8.78	9.79	11.33

Table 4.--*Effects of temperature on Van Waters and Rogers buffers*

[°C, degrees Celsius]

Temperature (°C)	pH (units)	Temperature (°C)	pH (units)	Temperature (°C)	pH (units)
VWR Catalog No. 34180-264 buffer solution pH 4					
0	4.01	20	4.00	40	4.03
10	4.00	25	4.01		
VWR Catalog No. 34180-297 buffer solution pH 7					
0	7.12	20	7.02	40	6.97
10	7.06	25	7.00		
VWR Catalog No. 34180-311 buffer solution pH 10					
0	10.33	20	10.05	30	9.95
10	10.20	25	10.00	40	9.89

7. Turn the meter switch from STANDBY to READ and using SLOPE adjustment on back side (SCREW) adjust pointer until it rests exactly on table value of pH 10 obtained in step 6. Turn meter to STANDBY, remove probe from buffer and rinse.

8. If sample alkalinity is to be measured or if sample pH is expected to be less than 7, then a pH 4 buffer is used for calibration in addition to the above. In calibration for pH 4, the same procedure is used as is described for calibration with pH 10.

9. After the instrument has been calibrated, rinse the electrode with deionized water and an aliquot of the water sample. Immerse the electrode in the water sample. NOTE: TURN THE METER TO STANDBY EACH TIME THE ELECTRODE IS REMOVED FROM A SOLUTION.

10. Measure the temperature of the water sample and adjust the TEMPERATURE dial to the corresponding temperature.

11. Turn meter to READ position and allow at least 3 minutes for the electrode to equilibrate with the sample. When sample reading is taken, sample needs to be in quiescent state. On any reading if meter needle does not stabilize within several minutes, outgassing or settling of charged suspended particles (clay) may be occurring. Outgassing can be reduced by placing the electrode into the sample container through a tightly fitting stopper. Normally, pH is measured on an unfiltered sample. However, if the sample contains appreciable suspended clay particles, slow settling of the clay particles may cause a continuous "drift" of the observed pH value. Such samples need to be filtered before the pH is determined. In dry windy climates, a static charge tends to build on the face of a pH meter, which causes erratic movement of the indicator needle. Polishing the face of the pH meter with a soft absorbent tissue containing several drops of antistatic solution will minimize this interference.

pH electrodes

Several types of combination electrodes, consisting of a glass electrode and reference electrode in one assembly, can be used. When the electrode is not in use, its tip is stored either in the electrolyte solution being used in the electrode or in distilled water (protect from freezing) so that the fiber junction will be maintained in a free-flowing condition and ready for use. For detailed care and maintenance of electrodes, see the manufacturer's instructions that accompany each electrode.

Before each field trip, the field person needs to check and, if necessary fill, the electrode with internal filling solution recommeded by the manufacturer.

[FILLING SOLUTIONS FOR DIFFERENT BRANDS OF
ELECTRODES ARE NOT INTERCHANGEABLE]

Personnel also need to complete a calibration check on the field meter with the appropriate electrodes and with pH 4, 7, and 10 buffers before each field trip to ensure that both the electrode and the meter are in proper working condition and again onsite, recording the calibration on the Field form.

[REGARDLESS OF THE TYPE OF METER OR ELECTRODE USED, NEVER REMOVE THE ELECTRODE FROM THE BUFFER OR SAMPLE UNLESS THE METER CONTROL IS IN THE "STANDBY" OR "OFF" POSITION]

pH buffers

Three standard buffers (pH 4, 7, and 10) usually will cover the range of pH for most surface waters and ground waters. Tables 2-4 indicate that the pH of each of these buffers is temperature dependent. A copy of the table for the appropriate buffer needs to be attached to the meter or the bottle containing that buffer for use in standardization of field instruments.

Alkalinity, total

Alkalinity is a measure of the buffering capacity of water against acid. Degasification, precipitation, and other chemical and physical reactions may cause the concentrations of carbonate and bicarbonate for some waters to change significantly within several hours or even minutes after sample collection. Consequently, field values for carbonate and bicarbonate or alkalinity usually are more reliable than values obtained in the laboratory.

Some of the techniques manuals of the Geological Survey have indicated that water samples for the determination of carbonate and bicarbonate not be filtered, diluted, concentrated, or altered in any way but that suspended material be allowed to settle before the sample is analyzed. For turbid waters that contain clays, consideration should be given to sample filtration prior to measurement of alkalinity.

Alkalinity is determined by titrating a water sample with a standard solution of sulfuric acid. The end point is selected as pH 4.5. Selection of this end point is arbitrary, and corresponds to the true equivalence point only under ideal conditions. The error generally is not serious for most surface water and ground water. However, if the carbonate and bicarbonate species are to be calculated and if precise alkalinity values are desired, then the "incremental method" is appropriate. Salts of weak organic acids, such as silicic, which cannot be corrected for, may yield erroneous results when present in large amounts. In addition, oils and greases, if present, may tend to foul the pH meter electrode and prevent its proper operation.

For a discussion of the factors involved in these and in more precise measurements of carbonate and bicarbonate, personnel are referred to "Guidelines for Collection and Field Analysis of Ground-Water Samples for Selected Unstable Constituents" (Wood, 1976).

Calibration of pH meter.--Use the meter that has been calibrated previously for pH measurement. (See section on pH.)

Field measurement.--

1. Fill 25-mL buret with 0.01639 N or a known normality sulfuric acid (H_2SO_4) solution.
2. Pipet 50 mL of filtered sample into a clean dry 100-mL beaker. The sample volume may be increased for low ionic strength solution or decreased for solutions of high ionic strength. (See section on filtration.)
3. Rinse pH electrode three times with an aliquot of the sample.
4. Insert pH electrode and a clean dry stirring bar into the sample.
5. Place beaker containing sample on the titration assembly and record the pH.
6. Adjust the stirrer speed to slow, titrate immediately to pH 4.5, and record the titrant volume on the field note sheet.

The calculation for total alkalinity (TA) as $CaCO_3$ in milligrams per liter is (titrant normality 0.06139):

$$TA = \frac{1{,}000}{\text{mL sample}} \times 0.8202 \times \text{mL titrant.} \qquad (6)$$

Report alkalinity concentrations as follows: Less than 10 mg/L, whole numbers; 10 -99 mg/L, two significant figures; more than 99 mg/L, three significant figures.

CAUTION

If the volume of titrant used in the determination exceeds 25 mL (size of buret from step 1), DO NOT refill buret and continue the titration. Select a smaller sample and repeat the procedure from step 3.

Alternative procedure for field determination of alkalinity

Apparatus

1. pH meter with combination pH probe or equivalent.
2. Digital titrator, with mounting assembly.
3. Titrant cartridges with bent-stem delivery tubes (normality of titrant will be 1.600 or 0.160).
4. Magnetic stirrer.
5. Demineralized water, Kimwipes
6. Sample holder.
7. 50-mL and 100-mL volumetric pipettes.

In this alternative method, a digital titrator is used in place of a buret. The titrant cartridge is inserted into the digital titrator and a delivery tube is attached to the cartridge. The pH electrode is inserted into the electrode assembly. Check to see that the magnetic stirrer has an appropriate power source and is working properly. The assembly is now ready to use. Before going into the field, the field person needs to study the digital-titrator methods manual and perform several "dry runs" in the office.

[BECOME THOROUGHLY FAMILIAR WITH THE OPERATION OF THE EQUIPMENT BEFORE ATTEMPTING TO USE IN THE FIELD]

A plunger in the digital titrator forces acid in the titrant cartridge into the delivery tube. The plunger is controlled by a main-drive screw, which in turn is controlled by rotation of the delivery knob. The delivery knob thus controls the titrant volume delivered and the digital counter. A digital-counter value of 800 is equal to 1 mL. Release a few drops of titrant from the end of the delivery tube, gently blot any droplets adhering to the end of the tube, and set the digital counter to a zero reading. Depending upon the expected alkalinity, select an appropriate strength titrant cartridge [0.1600 N (normal) H_2SO_4 or 1.600 N H_2SO_4]. A direct relationship is established between the digital-counter value for the equivalence point and the milligrams per liter of alkalinity as $CaCO_3$. Each digital-counter value is equal to 2.00 mg/L alkalinity as $CaCO_3$ for the 1.600 N H_2SO_4 titrant cartridge and 50 mL sample volume. If the sample volume is 100 mL and the acid concentration is 1.600 N H_2SO_4, then each digital-counter value is equal to 1.00 mg/L alkalinity as $CaCO_3$. If the alkalinity is known to be too small, then the 0.1600 N H_2SO_4 titrant cartridge is used. Each digital counter value is equal to 0.20 and 0.10 for 50 and 100 mL samples, respectively.

Calibrate the pH meter as usual and select a sample volume and titrant cartridge. Pour the measured sample volume into an appropriate size beaker for the titration and place the beaker so that the end of the delivery tube and the pH electrode are dipped below the surface of the sample. Record the pH value and insert stirring bar into the sample and turn on the magnetic stirrer. Rotate the delivery knob of the digital titrator so that a volume of acid is added to the sample. After each increment of acid is added to the sample, continue stirring for at least 30 seconds and then turn off stirrer and read the pH of the solution after the pH meter reading stabilizes. The pH of the sample solution is extremely sensitive to small additions of the acid (1.600 N). Therefore, be extremely careful after adding acid during the titration when the pH reads about 5.5. From pH readings of 5.5, add increments of acid by increasing the delivery knob by one or two counts until pH 4.5 is reached. Experience with the equipment will improve the operator's skill. Also, alkalinity concentrations at the regular water-quality stations can be estimated from the formula for the regression curves of conductivity and alkalinity. Report results as alkalinity in milligrams per liter as $CaCO_3$.

CALCULATIONS

1.600 N H_2SO_4

50 mL sample
mg/L alkalinity as $CaCO_3$ = Digital count x 2.00[a]

100 mL sample
mg/L alkalinity as $CaCO_3$ = Digital count x 1.00[b]

0.1600 N H_2SO_4

50 mL sample
mg/L alkalinity as $CaCO_3$ = Digital count x 0.20

100 mL sample
mg/L alkalinity as $CaCO_3$ = Digital count x 0.10

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[a] 2.44 x 0.8202 = 2.00
[b] 1.22 x 0.8202 = 1.00

Incremental titration for alkalinity, carbonate, and bicarbonate

Although a fixed end point (pH 4.5) titration is often used to determine alkalinity, accurate determination of alkalinity due to carbonate species, as well as determination of concentration of those species, must be measured by the incremental method of titration where the real end point can only be known after titration. The end points for titration of successive proton absorbing species are taken as the inflection points of the titration curve, or as the maximum rates of change of pH per volume of titrant added (fig. 7). Rather than the tedious process of constructing the curves to determine inflection points, simple computer programs are developed for this purpose, and it is only necessary to input the paired values of pH and volume of titrant in milliliters throughout a given range.

Procedure: The initial steps in this procedure are the same as those in the previous sections on alkalinity determinations. After the initial pH is measured, sample volume is measured, and the buret is filled, the procedures to be followed are:

1. Record the buret reading at the starting point.
2. If the pH is greater than 8.3, add acid titrant solution dropwise and carefully record the volume delivered in 0.02-mL increments (0.05-mL increments with a 25-mL buret) and record the pH after addition until pH is less than 8.0. Stir gently with magnetic stirrer or other appropriate stirring device while adding titrant and making readings. Allow 15-20 seconds for equilibrium after each acid addition.
3. If the initial pH is less than 8.3, skip step 2 and go directly to step 4.
4. Titrate rapidly to pH 5.0 and record the volume of titrant at pH 5.0 to the nearest 0.02 mL (0.05 mL for 25-mL buret).
5. From pH 5.0 to 4.0 add titrant in 0.02-mL increments (0.05-mL increments for 25-mL buret) and record the pH after each titration, allowing 15-20 seconds for pH equilibrium after each. The most sensitive part of the titration curve is usually between pH 4.8 and 4.3.

Calculation: The end points are obtained by constructing graphs for methods A or B in figure 7 or are the output of a computer computation after entering paired values of pH and volume of titrant in milliliters. For calculations it is necessary to determine the volume(s) of titrant from start to the end point(s).

1. Calculate carbonate

$$CO_3 (mg/L) = \frac{1,000}{mLs} \times (mLa \text{ at ep-1}) \times 0.9835 \qquad (7)$$

2. Calculate bicarbonate

$$HCO_3 \ (mg/L) = \frac{1,000}{mLs} \times (mLa \text{ at ep-2}) \times 1.00 \qquad (8)$$

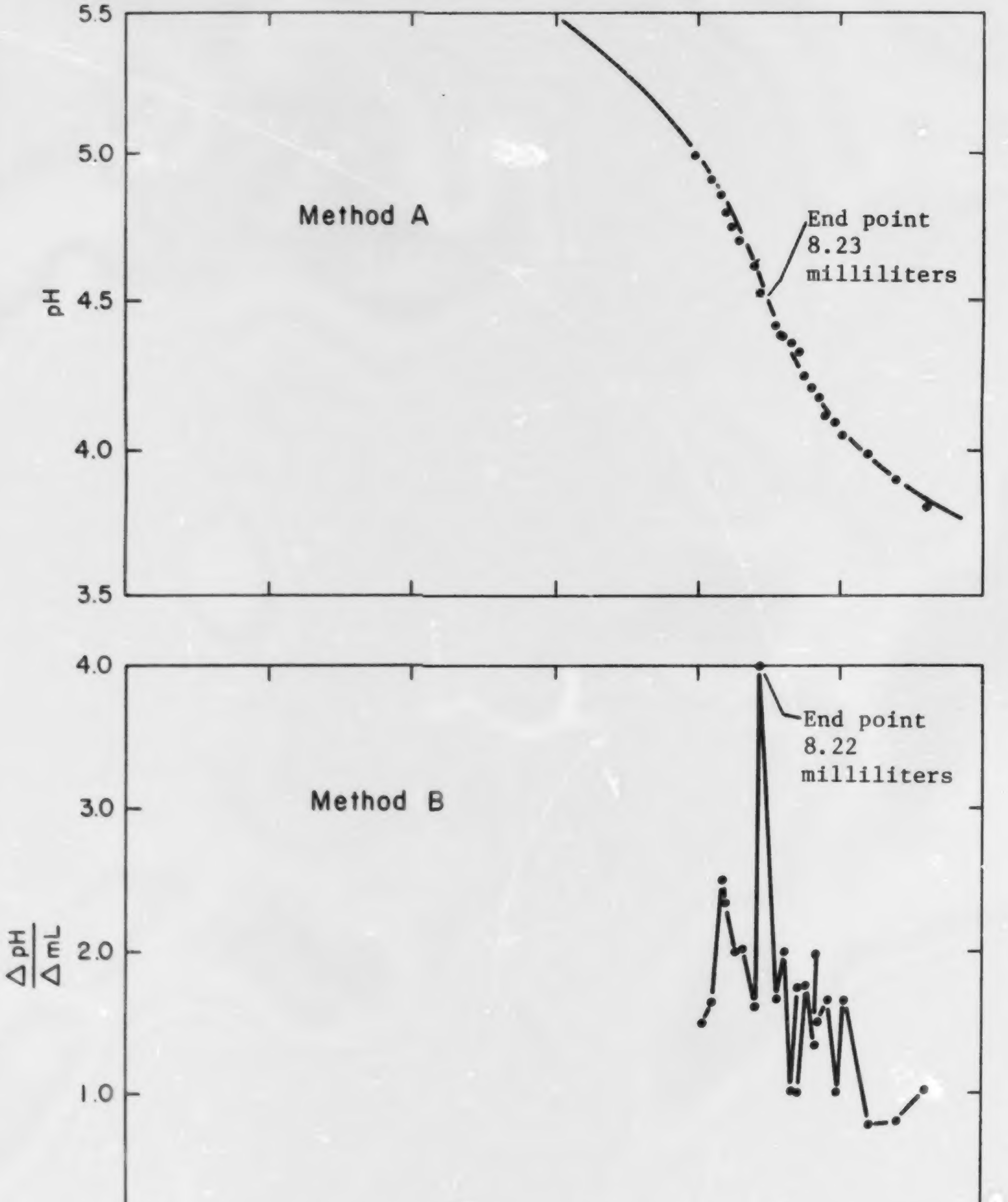

Figure 7.--Two methods of determining the end point for bicarbonate by incremental titration.

where

mLs = volume of sample, in milliliters;
mLa = volume of titrant added, in milliliters;
ep-1 = end point near pH 8.3; and
ep-2 = end point near pH 4.5.

Note: If the sulfuric acid standard solution has a normality different from 0.01639 N, compute new multiplying factors as follows:

$$\text{For } CO_3 \text{ factor} = 0.9835 \times \frac{\text{acid normality}}{0.01639\ N}$$

$$\text{For } HCO_3 \text{ factor} = 1.00 \times \frac{\text{acid normality}}{0.01639\ N}$$

3. Calculate carbonate alkalinity

$$\text{Alkalinity(mg/L as } CaCO_3) = \left[\frac{CO_3(\text{mg/L})}{30} \pm \frac{HCO_3(\text{mg/L})}{61}\right] \times 50.0 \qquad (9)$$

Reporting: report carbonate (90445), bicarbonate (90440) and carbonate alkalinity (90430) as follows: less than 1,000 mg/L, in whole numbers; 1,000 mg/L and greater, to three significant figures. For a more detailed discussion of the provisional method for the incremental titration of carbonate and bicarbonate in the field, see unpublished Quality of Water Branch Technical Memorandum 82.05.

Dissolved oxygen

General considerations

Oxygen dissolved in surface water is derived from the air and from the oxygen given off by aquatic plants in the process of photosynthesis. The solubility of oxygen in water is dependent upon the partial pressure of oxygen in the air, the temperature of the water, and the mineral content of the water. Dissolved oxygen in ground water usually is derived from contact with the atmosphere before recharge to the aquifer. Dissolved oxygen can exist at great depths in aquifers that have little or no oxidizable material in the water flow path.

The most commonly used methods for the determination of dissolved oxygen are the iodometric (Winkler) method (or modifications thereof) and the electrometric method. The iodometric method is a titrimetric procedure that is subject to certain interferences and, thus, is not applicable to a variety of waters containing industrial and domestic wastes. Extreme cold temperatures can create problems using the electrometric method. Both methods are described below.

Iodometric (modified Winkler) method

This method depends on the formation of a precipitate of manganous hydroxide. The oxygen dissolved in the water is rapidly absorbed by manganous hydroxide, forming a higher oxide, which may be in the following form:

$$MnSO_4 + 2\ KOH \rightarrow Mn(OH)_2 + K_2SO_4 \qquad (10)$$

$$2Mn(OH)_2 + O_2 \rightarrow 2MnO(OH)_2 \qquad (11)$$

The $Mn(OH)_2$ floc acts as a gathering agent for oxygen.

Upon acidification in the presence of iodide, iodine is released in a quantity equivalent to the dissolved oxygen present.

$$MnO(OH)_2 + 2KI + H_2O \rightarrow Mn(OH)_2 + I_2 + 2KOH \qquad (12)$$

The liberated iodine is then titrated with the standard sodium thiosulfate solution using starch indicator.

$$I_2 + 2S_2O_3^{-2} \rightarrow S_4O_6^{-2} + 2I^{-1} \qquad (13)$$

The method is applicable to samples which are not extensively polluted and is not used on samples containing more than 1 mg/L of ferrous iron or appreciable quantities of sulfite, thiosulfate, polythionate, hypochlorite, or free chlorine. In the following procedure, sodium-azide eliminates the interference of nitrite, and potassium fluoride overcomes the effect of ferric salts, provided the ferric iron concentration does not exceed 200 mg/L and titration is not delayed.

Procedure: Unless otherwise specified, a nonaerated sample is taken at midstream by the depth integrated method using BOD type samplers (described in the section, Sampling equipment selection and maintenance--Biochemical oxygen demand (BOD) samplers). Dissolved-oxygen samples from lakes and reservoirs are collected with Van Doren or Kemmerer type samplers. Samples are processed as follows:

1. To the nonaerated sample add 1 mL of potassium fluoride (KF) solution below the liquid surface of the sample in the BOD bottle. Stopper the bottle and mix.

2. Add 2 mL of manganous sulfate ($MnSO_4$) solution below the liquid surface of the sample, stopper the bottle, and mix.

3. Add 2 mL of alkali-iodide-azide reagent below the surface of the sample, stopper the bottle, and mix by inversion. Allow the precipitate to settle to the bottom one-third of the bottle, and then repeat the mixing and settling processes.

4. Add 2 mL of concentrated sulfuric acid (H_2SO_4) by allowing the acid to run down the neck of the bottle. Mix by gentle inversion until solution is complete.

5. Pipette (or using a volumetric flask) an aliquot of treated sample containing less than 2 mg oxygen (O_2) (200.00 mL maximum) and titrate the liberated iodine (I_2) with the standard solution (sodium thiosulfate or phenylarsine oxide) to a pale straw color.

6. Add 1 to 2 mL of starch indicator and continue the titration to the first disappearance of blue color. Subsequent recoloration can be disregarded.

7. Calculations are as follows:

$$DO\ (mg/L) = \frac{1,000}{A} \times \frac{B+5}{B} \times mL_t \times N_t \times 8 \qquad (14)$$

where

A = volume in milliliters from treated sample pipetted for titration,
B = total volume in milliliters of treated sample,
mL_t = volume in milliliters of titrant, and
N_t = normality of titrant

Note--When titrant normality is 0.0250 N, calculations can be simplified by selecting a treated sample volume of 101.67 mL. Under such circumstances the calculation is as follows:

$$DO(mg/L) = 2 \times mL_t \qquad (15)$$

Dissolved oxygen saturation in percent

Dissolved oxygen saturation in percent is automatically calculated in WATSTORE if values are entered for dissolved-oxygen concentration, water temperature, absolute barometric pressure, and specific conductance. However, this calculation also needs to be made in the field to determine if anomalous values have been measured. Oxygen solubility in milligrams per liter can be obtained from tables 5 and 6. Percent of saturation is calculated as follows:

$$\text{Oxygen Saturation (in percent)} = \frac{\text{measured dissolved oxygen}}{\text{table value for solubility}} \times 100 \qquad (16)$$

When saturation values become less than about 85 percent or more than 110 percent for an unknown reason, make a rerun determination for dissolved-oxygen concentration. If the values occur outside of this range for a known reason, a rerun may not be necessary. However, documentation of the reason must be recorded on the field notes. Example: "Station is below dam and percent saturation consistently is larger than 110 percent."

Note 1. Tables 5 and 6 are used to obtain solubility values for dissolved oxygen. Using table 5, a value is obtained from the point of intersection of water temperature in the vertical column and absolute barometric pressure in the horizontal column (interpolation between columns and rows may be necessary). This value is uncorrected for salinity. The solubility of oxygen in water decreases as salinity (specific conductance) increases. For this reason a correction factor from table 6 is applied to the value from table 5. As an example, the solubility is calculated for oxygen when the water temperature is 25°C, the atmospheric pressure is 660 mm of mercury, and the specific conductance is 5,000 microsiemens.

- From table 5 the uncorrected solubility value is 7.19 mg/L
- From table 6 the factor of 0.984 is obtained
- The corrected solubility value is then 7.19 mg/L x 0.984 = 7.08 mg/L

The 7.08 mg/L is the table value used to calculate percent of saturation.

Table 5.--*Solubility of oxygen in water at various temperatures and pressures*

[°C, degrees Celsius]

Temperature (°C)	Atmospheric pressure, in millimeters of mercury											
	710	700	690	680	670	660	650	640	630	620	610	600
	Solubility, in milligrams per liter											
0.0	13.67	13.47	13.28	13.08	12.89	12.70	12.50	12.31	12.12	11.92	11.73	11.53
0.5	13.47	13.28	13.09	12.90	12.71	12.51	12.31	12.13	11.94	11.75	11.56	11.37
1.0	13.28	13.09	12.90	12.71	12.53	12.34	12.15	11.96	11.77	11.58	11.40	11.21
1.5	13.09	12.91	12.72	12.54	12.35	12.17	11.98	11.79	11.61	11.42	11.24	11.05
2.0	12.91	12.73	12.55	12.36	12.18	12.00	11.81	11.63	11.45	11.26	11.08	10.90
2.5	12.74	12.56	12.38	12.20	12.01	11.83	11.65	11.47	11.29	11.11	10.93	10.75
3.0	12.57	12.39	12.21	12.03	11.85	11.67	11.50	11.32	11.14	10.96	10.79	10.60
3.5	12.40	12.22	12.05	11.87	11.70	11.52	11.34	11.17	10.99	10.82	10.64	10.46
4.0	12.24	12.06	11.89	11.72	11.54	11.37	11.19	11.02	10.85	10.67	10.50	10.32
4.5	12.08	11.91	11.74	11.56	11.39	11.22	11.05	10.88	10.71	10.53	10.36	10.19
5.0	11.92	11.75	11.58	11.42	11.25	11.08	10.91	10.74	10.57	10.40	10.23	10.06
5.5	11.77	11.61	11.44	11.27	11.10	10.94	10.77	10.60	10.43	10.27	10.10	9.93
6.0	11.63	11.46	11.29	11.13	10.96	10.80	10.63	10.47	10.30	10.14	9.97	9.81
6.5	11.48	11.32	11.15	10.99	10.83	10.66	10.50	10.34	10.17	10.01	9.85	9.68
7.0	11.34	11.18	11.02	10.86	10.69	10.53	10.37	10.21	10.05	9.89	9.73	9.56
7.5	11.20	11.04	10.88	10.72	10.56	10.41	10.25	10.09	9.93	9.77	9.61	9.45
8.0	11.07	10.91	10.75	10.60	10.44	10.28	10.12	9.96	9.81	9.65	9.49	9.33
8.5	10.94	10.78	10.62	10.47	10.31	10.16	10.00	9.85	9.69	9.53	9.38	9.22
9.0	10.81	10.65	10.50	10.35	10.19	10.04	9.88	9.73	9.58	9.42	9.27	9.11
9.5	10.68	10.53	10.38	10.22	10.07	9.92	9.77	9.62	9.46	9.31	9.16	9.01
10.0	10.56	10.41	10.26	10.11	9.96	9.81	9.65	9.50	9.35	9.20	9.05	8.90
10.5	10.44	10.29	10.14	9.99	9.84	9.69	9.54	9.39	9.25	9.10	8.95	8.80
11.0	10.32	10.17	10.03	9.88	9.73	9.58	9.44	9.29	9.14	8.99	8.85	8.70
11.5	10.20	10.06	9.91	9.77	9.62	9.48	9.33	9.18	9.04	8.89	8.75	8.60
12.0	10.09	9.95	9.80	9.66	9.51	9.37	9.23	9.08	8.94	8.79	8.65	8.50
12.5	9.98	9.84	9.69	9.55	9.41	9.27	9.12	8.98	8.84	8.69	8.55	8.41
13.0	9.87	9.73	9.59	9.45	9.31	9.16	9.02	8.88	8.74	8.60	8.46	8.32
13.5	9.76	9.62	9.48	9.34	9.20	9.06	8.92	8.78	8.64	8.51	8.37	8.23
14.0	9.66	9.52	9.38	9.24	9.10	8.97	8.83	8.69	8.55	8.41	8.27	8.14
14.5	9.56	9.42	9.28	9.14	9.01	8.87	8.73	8.60	8.46	8.32	8.19	8.05
15.0	9.45	9.32	9.18	9.05	8.91	8.78	8.64	8.51	8.37	8.23	8.10	7.96
15.5	9.36	9.22	9.09	8.95	8.82	8.68	8.55	8.42	8.28	8.15	8.01	7.88
16.0	9.26	9.12	8.99	8.86	8.73	8.59	8.46	8.33	8.19	8.06	7.93	7.80
16.5	9.16	9.03	8.90	8.77	8.64	8.50	8.37	8.24	8.11	7.98	7.85	7.71
17.0	9.07	8.94	8.81	8.68	8.55	8.42	8.29	8.16	8.02	7.89	7.76	7.63
17.5	8.98	8.85	8.72	8.59	8.46	8.33	8.20	8.07	7.94	7.81	7.68	7.55
18.0	8.88	8.76	8.63	8.50	8.37	8.25	8.12	7.99	7.86	7.73	7.61	7.48
18.5	8.80	8.67	8.54	8.42	8.29	8.16	8.04	7.91	7.78	7.65	7.53	7.40
19.0	8.71	8.58	8.46	8.33	8.21	8.08	7.95	7.83	7.70	7.58	7.45	7.33
19.5	8.62	8.50	8.37	8.25	8.12	8.00	7.87	7.75	7.63	7.50	7.38	7.25
20.0	8.54	8.41	8.29	8.17	8.04	7.92	7.80	7.67	7.55	7.43	7.30	7.18
20.5	8.45	8.33	8.21	8.09	7.96	7.84	7.72	7.60	7.48	7.35	7.23	7.11
21.0	8.37	8.25	8.13	8.01	7.89	7.76	7.64	7.52	7.40	7.28	7.16	7.04
21.5	8.29	8.17	8.05	7.93	7.81	7.69	7.57	7.45	7.33	7.21	7.09	6.97
22.0	8.21	8.09	7.97	7.85	7.73	7.61	7.50	7.38	7.26	7.14	7.02	6.90
22.5	8.13	8.01	7.90	7.78	7.66	7.54	7.42	7.31	7.19	7.07	6.95	6.83
23.0	8.05	7.94	7.82	7.70	7.59	7.47	7.35	7.24	7.12	7.00	6.88	6.77
23.5	7.98	7.86	7.75	7.63	7.51	7.40	7.28	7.17	7.05	6.93	6.82	6.70
24.0	7.90	7.79	7.67	7.56	7.44	7.33	7.21	7.10	6.98	6.87	6.75	6.64
24.5	7.83	7.71	7.60	7.49	7.37	7.26	7.14	7.03	6.92	6.80	6.69	6.57
25.0	7.75	7.64	7.53	7.42	7.30	7.19	7.08	6.96	6.85	6.74	6.62	6.51
25.5	7.68	7.57	7.46	7.35	7.23	7.12	7.01	6.90	6.79	6.67	6.56	6.45
26.0	7.61	7.50	7.39	7.28	7.17	7.06	6.94	6.83	6.72	6.61	6.50	6.39
26.5	7.54	7.43	7.32	7.21	7.10	6.99	6.88	6.77	6.66	6.55	6.44	6.33
27.0	7.47	7.36	7.25	7.14	7.03	6.92	6.82	6.71	6.60	6.49	6.38	6.27
27.5	7.40	7.29	7.19	7.08	6.97	6.86	6.75	6.64	6.54	6.43	6.32	6.21
28.0	7.34	7.23	7.12	7.01	6.91	6.80	6.69	6.58	6.47	6.37	6.26	6.15
28.5	7.27	7.16	7.06	6.95	6.84	6.74	6.63	6.52	6.41	6.31	6.20	6.09
29.0	7.20	7.10	6.99	6.89	6.78	6.67	6.57	6.46	6.36	6.25	6.14	6.04
29.5	7.14	7.03	6.93	6.82	6.72	6.61	6.51	6.40	6.30	6.19	6.09	5.98
30.0	7.07	6.97	6.87	6.76	6.66	6.55	6.45	6.34	6.24	6.14	6.03	5.93
	1840	2230	2630	3030	3430	3840	4250	4670	5100	5540	5980	6430

ELEVATION, IN FEET ABOVE SEA LEVEL

Table 6.--*Salinity correction factor*[1] *for dissolved oxygen in water based on specific conductance*

[°C, degrees Celsius]

Temperature (°C)		Specific conductance, in microsiemens per centimeter at 25°C								
		0	1,000	2,000	3,000	4,000	5,000	6,000	7,000	8,000
0.0	*	1.000	0.996	0.992	0.989	0.985	0.981	0.977	0.973	0.969
1.0	*	1.000	0.996	0.992	0.989	0.985	0.981	0.977	0.973	0.969
2.0	*	1.000	0.996	0.992	0.989	0.985	0.981	0.977	0.973	0.970
3.0	*	1.000	0.996	0.993	0.989	0.985	0.981	0.977	0.974	0.970
4.0	*	1.000	0.996	0.993	0.989	0.985	0.981	0.978	0.974	0.970
	*									
5.0	*	1.000	0.996	0.993	0.989	0.985	0.981	0.978	0.974	0.970
6.0	*	1.000	0.996	0.993	0.989	0.985	0.982	0.978	0.974	0.970
7.0	*	1.000	0.996	0.993	0.989	0.985	0.982	0.978	0.974	0.971
8.0	*	1.000	0.996	0.993	0.989	0.986	0.982	0.978	0.975	0.971
9.0	*	1.000	0.996	0.993	0.989	0.986	0.982	0.978	0.975	0.971
	*									
10.0	*	1.000	0.996	0.993	0.989	0.986	0.982	0.979	0.975	0.971
11.0	*	1.000	0.996	0.993	0.989	0.986	0.982	0.979	0.975	0.971
12.0	*	1.000	0.997	0.993	0.989	0.986	0.982	0.979	0.975	0.972
13.0	*	1.000	0.997	0.993	0.990	0.986	0.983	0.979	0.975	0.972
14.0	*	1.000	0.997	0.993	0.990	0.986	0.983	0.979	0.976	0.972
	*									
15.0	*	1.000	0.997	0.993	0.990	0.986	0.983	0.979	0.976	0.972
16.0	*	1.000	0.997	0.993	0.990	0.986	0.983	0.979	0.976	0.972
17.0	*	1.000	0.997	0.993	0.990	0.986	0.983	0.980	0.976	0.973
18.0	*	1.000	0.997	0.993	0.990	0.987	0.983	0.980	0.976	0.973
19.0	*	1.000	0.997	0.993	0.990	0.987	0.983	0.980	0.976	0.973
	*									
20.0	*	1.000	0.997	0.993	0.990	0.987	0.983	0.980	0.977	0.973
21.0	*	1.000	0.997	0.993	0.990	0.987	0.984	0.980	0.977	0.973
22.0	*	1.000	0.997	0.993	0.990	0.987	0.984	0.980	0.977	0.974
23.0	*	1.000	0.997	0.994	0.990	0.987	0.984	0.980	0.977	0.974
24.0	*	1.000	0.997	0.994	0.990	0.987	0.984	0.981	0.977	0.974
	*									
25.0	*	1.000	0.997	0.994	0.990	0.987	0.984	0.981	0.977	0.974
26.0	*	1.000	0.997	0.994	0.990	0.987	0.984	0.981	0.978	0.974
27.0	*	1.000	0.997	0.994	0.991	0.987	0.984	0.981	0.978	0.975
28.0	*	1.000	0.997	0.994	0.991	0.987	0.984	0.981	0.978	0.975
29.0	*	1.000	0.997	0.994	0.991	0.988	0.984	0.981	0.978	0.975
	*									
30.0	*	1.000	0.997	0.994	0.991	0.988	0.985	0.981	0.978	0.975

[1] From Weiss (1970, p. 71).

Electrometric method

The field method commonly used for measuring dissolved oxygen is the electrometric (instrument) method, which utilizes a membrane-type dissolved-oxygen electrode. The membrane passes oxygen at a rate that is directly proportional to the partial pressure of oxygen in solution outside the membrane. When oxygen diffuses through the membrane, it is rapidly consumed at the cathode. The consumption of oxygen causes a current to flow through the cell. The current is directly proportional to the quantity of oxygen consumed and can be converted to concentration units by calibration procedures. The membrane is permeable to gases other than oxygen. Halogens, hydrogen sulfide, sulfur dioxide, and helium interfere, and hydrogen sulfide poisons the electrode. For a more thorough discussion concerning the principles of the electrometric method of measuring dissolved oxygen, see "Methods for Determination of Inorganic Substances in Water and Fluvial Sediments" (Skougstad and others, 1979).

The following sections outline the methods of instrument calibration and field measurement of dissolved oxygen with the YSI Model 54 oxygen meter. For methods of operating other instruments, refer to the instruction manuals provided by the manufacturer.

Preparation of oxygen probe.--Field probes commonly used are the YSI 5739 nonstirring in situ probe and the YSI 5750 nonstirring BOD bottle probe. After the probes have been prepared for field use, the membranes will last indefinitely, depending on usage. However, if the electrolyte is allowed to evaporate and (or) an excessive amount of bubbles forms under the membrane, or the membrane becomes damaged, the membrane must be removed, the reservoir flushed with potassium chloride (KCl) electrolyte, and a new membrane installed. The membrane is also to be replaced if readings become erratic or calibration is unstable. The method of probe preparation is as follows:

1. Prepare the electrolyte by dissolving with distilled water the KCl crystals from the standard kit in the 30-mL dropper bottle. (Fill the bottle to the top.)

2. Unscrew the sensor guard from the bottom of the probe (YSI 5739 probe only) and remove the O ring and membrane.

3. The gold cathode at the probe tip should always be bright and untarnished. To clean, wipe with a clean lint-free cloth or hard paper. Never use abrasives or chemicals.

4. Thoroughly rinse the sensor tip with KCl solution. Invert the probe, fill with electrolyte, and apply a membrane as follows:

    a. Grasp the probe with the left hand. When preparing the YSI 5739 probe, the pressure compensating vent needs to be to the right. Fill the sensor body at the tip of the probe with KCl electrolyte by pumping the diaphragm near the middle of the probe with an eraser end of a pencil or similar soft, blunt tool. Continue filling and pumping until no more air bubbles appear. The 5750 BOD bottle probe does not have a diaphragm and can be filled simply by adding KCl solution until no air bubbles appear.

    b. Remove a membrane from the kit. Secure the membrane between left thumb and side of probe near the probe tip. Add more electrolyte to the probe tip until the electrolyte completely covers the tip. Handle membrane only at ends, keeping it clean and dust free.

    c. Grasp the free end of the membrane with the thumb and forefinger of right hand. With one continuous motion, stretch the membrane up and over the probe tip and down the other side.

    d. Secure the end of the membrane under the forefinger of the left hand holding the probe.

    e. Roll the O ring over the end of the probe. There should be no wrinkles in the membrane or air bubbles trapped under the membrane. Wrinkles can be removed by tugging lightly on the edges of the membrane beyond the O ring.

f. Trim off excess membrane with scissors or sharp knife. Check that the stainless steel temperature sensor is not covered by excess membrane.

5. Replace the sensor guard (YSI 5739 probe only).

Field calibration of DO meter

The following section discusses procedures for calibrating the oxygen meter. These procedures, listed in order of preference, are: (1) air calibration chamber in water; (2) calibration by Winkler titration; (3) calibration with air-saturated water; and (4) air calibration chamber in air.

Air calibration chamber in water.--The air calibration chamber (YSI Model 5075, or equivalent) permits calibration of the oxygen meter at the temperature of the water in which the DO content is to be measured, thereby minimizing errors due to temperature differences. Dip the calibration chamber into the water; pour out excess water, and then insert DO probe into the wet chamber. This ensures that the air inside the chamber is saturated with water vapor.

Caution: Be sure that no water can leak into the calibration chamber and that the membrane has no droplets of water adhering to it, because this would reduce the rate of oxygen diffusion through the membrane. It also would produce erroneous results.

1. Place calibration chamber in the water in which the DO content is to be measured. Allow 10 to 15 minutes for the temperature of the air inside the chamber to equilibrate with the water.

The calibration chamber (Model 5075) is designed to allow the membrane surface of the DO probe (Model 5739) to be at ambient atmospheric pressure while in the chamber, but unless the chamber has been modified it is not large enough for the entire DO probe and pressure compensator to fit inside (See unpublished Quality of Water Branch Technical Memorandum No. 79.08(B) for modification). Because the pressure compensator must remain at atmospheric pressure, care must be taken to ensure that the pressure compensator is not submerged below the water surface if this method is used. If modification has been made, the entire chamber and probe unit can be submerged.

2. Read the absolute atmospheric pressure from pocket altimeter-barometer to the nearest 1 mm of mercury.

3. Recheck the REDLINE and ZERO reading on the oxygen meter and adjust if necessary.

4. Measure temperature in the calibration chamber to the nearest 0.5°C, using the thermistor in the DO probe.

5. Using oxygen solubility (table 5), determine the DO saturation value at the measured water temperature and absolute atmospheric pressure.

6. Select the scale (0-10 mg/L or 0-20 mg/L) to be used for the DO measurement and adjust CALIBRATION control until meter reads the DO saturation value determined in the oxygen solubility table. Do not change scales without recalibrating meter or verifying that identical readings are obtained on both scales. Meter is now calibrated and ready for use.

Calibration by Winkler titration: The DO meter is calibrated with distilled or deionized water in which the DO concentration has been determined by the Winkler method.

1. Place 1 to 2 liters of distilled or deionized water in a large container. The water preferably is to be near saturation with respect to DO and the water temperature reasonably close to the ambient temperature. These conditions should ensure that the DO concentration in the distilled water remains constant.

2. Place DO probe in the distilled water. Maintain a velocity of at least 1 ft/s past the DO probe with a magnetic stirrer or other means.

3. Check ZERO and REDLINE, and adjust if necessary.

4. Switch meter to the appropriate scale and adjust reading to the approximate DO concentration with the calibration control.

5. After DO meter has stabilized, determine the DO concentration of two aliquots of the distilled water by the Winkler titration procedure as previously described. If results of the two Winkler titrations do not agree within 0.1 mg/L, the titration needs to be repeated.

6. Without delay recheck ZERO and REDLINE then adjust CALIBRATION control until DO meter reads DO concentration determined. Meter is now calibrated and ready for use.

Calibration with air-saturated water: The DO meter is calibrated against water which is saturated with oxygen at a known temperature and true atmospheric pressure. Obtain approximately 1 liter of distilled water or water from the water body to be measured. The temperature of the water used for calibration is to be close to ambient temperature so there is no heating or cooling.

1. Place DO probe and the calibration water in a large beaker or open-mouth container and allow the probe to come to thermal equilibrium. Shield beaker from direct sunlight and wind to minimize temperature variations.

2. Aerate the water for 5 to 10 minutes. Aeration is most easily accomplished with a small battery-operated aquarium pump or minnow bucket aerator and a short section of tubing. A gas diffusion stone needs to be attached to the end of the tubing and placed at the bottom of the beaker of calibration water.

3. It is extremely important to ensure that the water is 100 percent saturated with oxygen. An indication of 100 percent saturation can be determined as follows. Switch DO meter to the 0-10 mg/L scale and adjust meter reading to approximately 8 mg/L with the CALIBRATION control. Observe meter while areating calibration water. When no change in DO reading on meter is observed for 4 to 5 minutes, the water can be assumed to be saturated.

4. Read true atmospheric pressure from pocket altimeter-barometer to the nearest 1 mm of mercury.

5. Recheck the REDLINE and ZERO reading on the oxygen meter and adjust if necessary.

6. Measure temperature of the calibration water to the nearest 0.5°C.

7. Using the oxygen solubility table, determine the DO solubility value at the measured water temperature and absolute atmospheric pressure. Apply a salinity correction if necessary.

8. Select the scale (0-10 mg/L or 0-20 mg/L) to be used for the DO measurement. Turn off aerator and adjust CALIBRATION control until meter reads the DO solubility value determined above. Do not change scales without recalibrating meter or verifying that identical readings are obtained on both scales. Meter is now calibrated and ready for use.

Note 2. It is essential that calibration be completed with the temperature of the calibration water at the value measured, otherwise the calibration water may be undersaturated or oversaturated with oxygen. If the temperature changes or later recalibration of the meter is necessary, the calibration procedure must be repeated.

Air calibration chamber in air: This procedure is similar to the procedure described in air calibration chamber in water, except that calibration is performed with the air calibration chamber in air rather than in water. This procedure can be used only with probes that have the temperature sensing thermistor located adjacent to the membrane. The probe must be capable of automatically compensating for temperature changes. However, this procedure is not to be used if the air temperature differs from the water temperature by more than 10°C. Also, the calibration chamber must be shielded from direct sunlight and wind to avoid large temperature fluctuations.

1. Wet the inside of the calibration chamber with water; pour out the excess water and insert the probe into the wet chamber. This ensures 100 percent humidity. Allow sufficient time (10 to 15 minutes) for the DO probe and air inside the calibration chamber to equilibrate.
2. Read true atmospheric pressure from pocket altimeter-barometer to the nearest 1 mm of mercury.
3. Recheck the REDLINE and ZERO readings on the oxygen meter and adjust if necessary.
4. Measure temperature in the calibration chamber to the nearest 0.5°C using the thermistor in the DO probe.
5. Using the oxygen solubility table, determine the DO saturation at the measured temperature and true atmospheric pressure.
6. Select the scale (0-10 mg/L or 0-20 mg/L) to be used for the DO measurement and adjust CALIBRATION control until the meter reading is at the DO saturation value determined from the solubility table. Do not change scales without recalibrating meter or verifying that identical readings are obtained on both scales. Meter is now calibrated and ready for use.

Making the measurement

In situ measurement.--If dissolved oxygen is to be measured in situ, the probe needs to be immersed directly in the stream near the center of flow. If the velocity of the stream at the point of measurement is less than about 1 ft/s, manual stirring must be provided by raising or lowering the probe about 1 ft/s. (Do not break the surface of the water.) If the stream velocity is so great that the probe cannot be submerged, the probe can be attached to a sounding weight on a separate line and the sounding weight and probe submerged. (Do not support the sounding weight with the probe cable!)

After the probe has been submerged and the stirring rate of at least 1 ft/s has been established, complete the dissolved-oxygen measurement as follows:

1. Turn operation switch to the 0-20 mg/L range.

2. After the reading on the meter has stabilized (at least 2 minutes), read and record the dissolved-oxygen values of less than 20.0 mg/L to the nearest 0.1 mg/L. If the value exceeds 20 mg/L, record ">20 mg/L." To express the results as "percent saturation," see section "Field measurement methods, Dissolved oxygen, Dissolved oxygen saturation in percent." For values of dissolved oxygen less than 10 mg/L, the 0-10 scale provides greater accuracy. It must be remembered, however, that each scale used requires calibration as previously described.

3. Turn the operation switch to the OFF position.

4. Remove the probe from the water, rinse with deionized water, and store with the probe tip immersed in deionized water. (Protect from freezing!)

Measurement of DO from sample in BOD bottle.--In situ measurement of dissolved oxygen is impractical in some instances (for example, during thunderstorms or adverse weather conditions that might damage the instrument). Under such circumstances, an unaerated sample for the measurement of dissolved oxygen may be collected with a BOD sampler. (Dissolved oxygen is never measured on subsamples from the Geological Survey churn splitter.)

If a BOD sampler is to be used, the sample is collected and dissolved oxygen measured as follows:

1. Insert BOD bottle containing a magnetic stirring bar into BOD sampler.

2. Lower BOD sampler in a vertical near the centroid of flow. Allow several minutes for temperature of sampler to equilibrate with that of the stream.

3. Remove sampler from stream and empty. (If stream velocity is too great to completely submerge sampler, add sounding weight.)

4. Lower sampler into stream. Carefully raise and lower the sampler without breaking the water surface until escape of air bubbles ceases. (If sampler breaks water surface before escape of air bubbles ceases, sample will be aerated and must be discarded).

5. After escape of air bubbles ceases, remove sampler from stream, transport to field vehicle, and begin dissolved-oxygen measurement immediately, before temperature changes.

6. Remove top section from BOD sampler. Without removing BOD bottle from sampler, insert YSI 5750 probe into BOD bottle. (YSI 5739 probe cannot be used unless it has been modified to fit tapered BOD bottles.)

7. Remove BOD bottle containing the sample, magnetic stirring bar, and DO probe from the sampler and place on magnetic stirrer (BOD probes are also available with built-in stirrers).

8. Turn operation switch on the oxygen meter to the 0-20 mg/L range or, for small values of dissolved oxygen, the 0-10 mg/L range.

9. Turn on magnetic stirrer and adjust the stirrer speed until deflection on the meter is maximum.

10. Allow the meter to stabilize (at least 2 minutes). Read and record the dissolved-oxygen value of less than 20.0 mg/L to the nearest 0.1 mg/L. If the value exceeds 20 mg/L, record ">20 mg/L."

11. Turn the operation switch to the OFF position.

12. Remove the probe from the sample, rinse with deionized water, and store with the probe tip immersed in deionized water. (Protect from freezing.).

13. To express the results of dissolved-oxygen measurements as "percent saturation" see the section entitled, "Dissolved oxygen saturation in percent."

Bacteriological analyses

General considerations

Bacteriological analyses of water commonly include one or more of the determinations for total coliform, fecal coliform, and fecal streptococcal bacteria.

For the purpose of the method described in this section, the coliform group is defined as all the organisms that produce colonies having a golden-green metallic sheen within 24 hours when incubated at 35°C ± 0.5°C on M-Endo medium. The fecal coliform group is all the organisms that produce blue colonies within 24 hours when incubated at 44.5°C ± 0.2°C on M-FC medium. The fecal streptococcal group is all the organisms that produce red or pink colonies within 48 hours when incubated at 35°C ± 0.5°C on KF streptococcal medium.

The coliform group of bacteria has been the principal indicator of the suitability of a particular water for domestic, dietetic, and similar uses. The concentration of these bacteria indicates the degree of contamination of the water with wastes from human or animal sources. Traditionally, use has been made of tests for the detection and enumeration of these indicator organisms rather than pathogens. Increasing attention is being given to the potential value of fecal streptococcal bacteria as indicators of significant pollution of water.

The standard tests for the presence of total coliform, fecal coliform, and fecal streptococcal bacteria can be conducted using membrane-filter techniques or by multiple-tube fermentation techniques. Tests used by the U.S. Geological Survey in the field are the membrane-filter techniques, which are described in the following sections and are discussed in more detail in the report, "Methods for the Collection and Analysis of Aquatic Biological and Microbiological Samples" (Greeson and others, 1977). The multiple-tube fermentation techniques, significance of bacteriological determinations, and environmental factors are discussed in "Standard methods for the examination of water and wastewater," (American Public Health Association and others, 1981).

To date, limits have not been universally established on allowable numbers of indicator organisms in different waters, other than those that apply to the total and fecal coliform groups. These data are only a guide, because local standards vary. Where they differ, the local standards, are to be used.

The fecal coliform/fecal streptococcal ratio (FC/FS) can be a useful indicator in stream pollution studies to indicate the origin of human/animal contamination. Numerous investigations have shown that animals other than man harbor in their gastro-intestinal tract more fecal streptococcal than fecal coliform bacteria. The reverse is true in man. In examinations made on human and animal feces over a 24-hour period, the FC/FS ratio in man was usually greater than 4, whereas that in animals was less than 0.7. Various ratios can be interpreted as shown in table 7.

Table 7.--*Ratios between fecal coliform and fecal streptococcal bacteria used to determine the source of contamination*

[≤, equal to or less than; ≥, equal to or more than]

FC/FS ratio	Potential bacterial source
≤ 0.7	Livestock or poultry
0.7 - 1.0	Mixed pollution predominated by either livestock or poultry wastes
1 - 2	Mixed pollution of uncertain sources
2 - 3	Mixed pollution with probable human wastes
3 - 4	Mixed pollution predominated by human wastes
≥ 4	Human wastes

The following conditions are required for results to be statistically valid:

1. The fecal streptococcal count is greater than 25 colonies/100 mL.

2. The range of the pH of the source water is within 4.0-9.0. (Bacterial survival is affected by very high or very low pH.)

3. Fecal coliform is the only bacteria count used to determine a valid ratio. (Total coliform includes far too many non-fecal bacteria.)

4. Samples are collected no more than 24 hours travel time downstream from the sources of pollution. (After 24 hours, problems with bacterial die-off obscure interpretation of ratios.

5. Samples are collected from the same sources at the same time.

According to the U.S. Environmental Protection Agency (1977) for community and noncommunity water systems, when the filter membrane technique is used the number of total coliform bacteria shall not exceed the following:

a. One per 100 mL as the arithmetic mean of all samples examined, or

b. Four per 100 mL in more than 1 sample when less than 20 are examined per month, or

c. Four per 100 mL in more than 5 percent of the samples when 1 or more are examined per month.

Glassware sterilization

Glassware is sterilized by autoclaving for 20 minutes at 121°C at 15 lb/in^2. Except when in metal containers, glassware can be sterilized in a hot-air oven for not less than 1 hour at a temperature of 170°C. Glassware in metal containers may be sterilized at 170°C for not less than 2 hours.

Buffered dilution water

Dilution of samples for bacteriological examination are to be made with sterile, buffered, dilution water. To prepare the stock buffer solution, dissolve 34.0 grams potassium dihydrogen phosphate (KH_2PO_4) in 500 mL of distilled water. Adjust to pH 7.2 with a 1 N solution of sodium hydroxide (NaOH). Dilute to 1 liter with distilled water. Sterilize (autoclave) in a glass bottle for 20 minutes at 121°C at 15 lb/in^2. If an autoclave is not available, the solution can be sterilized in a covered glass beaker by boiling for 30 minutes or by filtering with a sterile membrane filter into a sterile glass bottle. After a bottle of this stock solution is opened for use, the unused part will need to be refrigerated. Discard contaminated solutions, indicated by turbidity or precipitate accumulation.

To prepare the sterile, buffered dilution water, add 1.2 mL of the stock phosphate buffer solution to 1 liter of distilled water containing 1 g (gram) of Difco peptone (0118) or equivalent. Sterilize (autoclave) in a glass bottle for 20 minutes at 121°C at 15 lb/in^2. If an autoclave is not available, the solution can be sterilized in a covered glass beaker by boiling for 30 minutes or by filtering aseptically through a sterile membrane filter. Dispense 99 2.0-mL portions in sterile glass dilution bottles. Buffer dilution water can also be obtained from specified Geological Survey water-quality laboratories.

Total coliform bacteria--Membrane-filter method

Preparation of M-Endo agar medium.--Reagents for preparation of M-Endo agar medium can be purchased from specified Geological Survey water-quality laboratories. A total coliform medium kit obtained from the laboratory consists of two packets. The reagents contained in each packet are sufficient to prepare 100 mL of M-Endo medium (enough to pour 15 plates). The following procedure is used for preparation of medium from the reagents.

1. Empty the vial containing dehydrated agar into a 250-mL beaker and add a 2-percent ethanol solution (100 mL).
2. Stir the mixture well for several minutes to dissolve clumps and to prevent agar from adhering to the beaker.
3. Place the beaker on a hot plate or "Hot Pot" (do not autoclave) and heat slowly to boiling. Stir the mixture constantly to prevent scorching.
4. When the medium just reaches the boiling point (95-96°C), promptly remove from heat. Do not boil!
5. Cool the medium to a temperature of 45° to 50°C and pour to a depth of about 3/16 inch (6 to 7 mL) in 50-mm petri dish bottoms (to the ridge of the plates).
6. When the medium has solidified, place the petri dish tops on tightly. The plates are suitable for use after the medium has solidified.
7. Plates that are not used immediately after preparation need to be placed in small plastic bags to prevent drying and can be stored in darkness in an ice chest or refrigerator (2° to 10°C) for a maximum of 5 days.

Fecal coliform bacteria--Membrane-filter method

Preparation of M-FC agar medium.--Reagents for preparation of M-FC agar medium can be purchased from specified Geological Survey water-quality laboratories. A fecal coliform medium kit obtained from the laboratory consists of two packets. The reagents contained in each packet are sufficient to prepare 100 mL of M-FC agar (enough to pour 15 plates). The following procedure is used for preparation of medium from these reagents.

1. Prepare the rosolic acid solution first by adding 10 mL NaOH (sodium hydroxide) to the rosolic acid crystals. Shake the mixture to dissolve crystals. Do not heat!
2. Empty the vial containing dehydrated agar into a 250-mL beaker and add distilled water (100 mL).

3. Stir the mixture well for several minutes to dissolve clumps and to prevent agar from adhering to the beaker.

4. Place the beaker on a hot plate or "Hot Pot" and heat slowly to boiling. Stir the mixture constantly to prevent scorching.

5. With a clean pipet, add 1 mL rosolic acid solution. Stir and continue heating for 1 minute.

6. Cool the medium to a temperature of 45° to 50°C and pour to a depth of about 3/16 inch (6 to 7 mL) in 50-mm petri dish bottoms (to the ridge of the plates).

7. When the medium has solidified, replace petri dish tops tightly. The plates are suitable for use after the medium has solidified.

8. Plates that are not used immediately after preparation need to be placed in small plastic bags to prevent drying and can be stored in darkness in an ice chest or refrigerator (2° to 10°C) for a maximum of 3 days. Preferably, the medium is not stored for more than 24 hours.

Fecal streptococcal bacteria--Membrane-filter method

Preparation of KF streptococcus agar medium.--Reagents for preparation of KF streptococcus agar medium can be purchased from specified Geological Survey water-quality laboratories. A fecal streptococcus medium kit obtained from the laboratory consists of two packets. The reagents contained in each packet are sufficient to prepare 100 mL of KF streptococcus agar medium (enough to pour 15 plates). The following procedure is used for preparation of medium from these reagents.

1. Empty the vial containing dehydrated agar into a 250-mL beaker and add distilled water (100 mL).

2. Stir the mixture well for several minutes to dissolve clumps and to prevent agar from adhering to the beaker.

3. Add 10 mL of distilled water to the TTC (triphenyltetrazolium chloride). Sterilize the TTC solution by aseptically filtering through a disposable sterile membrane filter (0.22 micrometer) into a sterile dilution bottle. Do not heat.

4. Place the beaker containing the agar solution on a hot plate or "Hot Pot" and heat slowly to boiling. Stir the mixture constantly to prevent scorching. After boiling begins, heat at this temperature for 5 minutes.

5. Remove agar solution from heat and cool to 50°-60°C. With a sterile pipet, add 1 mL of sterile TTC solution and stir.

6. Cool the medium to a temperature of about 50°C and pour to a depth of about 3/16 inch (6-7 mL) in 50-mm petri dish bottoms (to the ridge of the plates).

7. When the medium has solidified, replace petri dish tops tightly. The plates are suitable for use after the medium has solidified.

8. Plates that are not used immediately after preparation need to be placed in small plastic bags to prevent drying and can be stored in darkness in an ice chest or refrigerator (2° to 10°C) for a maximum of 2 weeks.

Sample collection

Samples for bacteriological examination are collected in clean, sterile bottles. Field sterilization of depth-integrating water-sediment samplers is impractical; consequently, these samplers are not be used for the collection of bacteriological samples.

Samples from shallow streams are collected from a single vertical near the centroid of flow by wading. When collecting the sample, the field person faces upstream, holding the bottle near its base and immersing the bottle with the mouth directed toward the current.

Samples from deep streams can be collected from a bridge or cableway with a weighted bottle (tubular insert sampler) by immersing the sampler at a single vertical near the centroid of flow. The empty sampler is immersed in the stream before the sample bottle is inserted to avoid the possibility of contamination of the sample. When the sample is collected, air space is left in the bottle to facilitate mixing of the sample.

[THE CHURN SAMPLE SPLITTER SHOULD NOT BE USED IN BACTERIA SAMPLING]

Sample preservation

Bacteriological determinations are started as soon as possible after sample collection, preferably within 1 hour and not more than 6 hours after sample collection. Samples must be chilled on ice during the time between collection and filtration. (Do not freeze.)

Residual chlorine in a water sample will destroy the biological population and may prevent an accurate determination of bacteria in the sample, unless the chlorine is destroyed at the time of sample collection. Therefore, if a sample from a halogenated water supply is taken, 1.0 mL of 10-percent solution of sodium thiosulfate needs to be added to the 1-liter sample bottle after sample collection. This reagent, which will neutralize about 15 mg/L of residual chlorine in the sample, shows no effect upon viability or growth.

Selection of sample volumes

The volume of sample to be filtered needs to be such that after incubation one of the plates will contain the following:

Total coliform - 20 to 80 colonies
Fecal coliform - 20 to 60 colonies
Fecal streptococcus - 20 to 100 colonies

In some instances it is difficult, if not impossible, to process a sample volume large enough to provide the minimum plate count (20 colonies). For routine field work with raw water, the maximum sample volume can be 100 mL.

The selection of sample volume is sometimes difficult to determine unless prior sampling has given an indication of bacteria densities. Five plates with selected sample volumes can usually give a coverage that will provide at least one plate within the ideal range (unless stream bacteria densities are very small). The following sample volumes can be used when no prior experience exists.

1. Total coliform
    a. Unpolluted raw surface water: Sample volumes of 0.25, 1.0, 5.0, 25.0, and 100.0 mL will cover a range of 20 to 32,000 colonies per 100 mL.
    b. Polluted raw surface water: Sample volumes of 0.001, 0.004, 0.016, 0.064, and 0.25 mL will cover a range of 8,000 to 8,000,000 colonies per 100 mL.
2. Fecal coliform
    a. Unpolluted raw surface water: Sample volumes of 1.0, 3.0, 10.0, 30.0, and 100.0 mL will cover a range of 20 to 6,000 colonies per 100 mL.
    b. Polluted raw surface water: Sample volumes of 0.001, 0.003, 0.01, 0.03, and 1.0 mL will cover a range of 2,000 to 6,000,000 colonies per 100 mL.
3. Fecal streptococci
    a. Unpolluted raw surface water: Sample volumes of 0.20, 1.0, 5.0, 25.0, and 100.0 mL will cover a range of 20 to 50,000 colonies per 100 mL.
    b. Polluted raw surface water: Sample volumes of 0.0005, 0.002, 0.01, 0.05, and 0.20 mL will cover a range of 10,000 to 20,000,000 colonies per 100 mL.

Analytical procedures

After the sample has been collected and the appropriate volumes of sample to be filtered have been selected, label the petri dishes with the station number and the volume to be filtered and proceed with the analysis.

1. Sterilize the filter apparatus as follows:
    a. Remove the stainless steel receiver flask from the base assembly.
    b. Saturate the asbestos ring (wick) around the base assembly with methanol.

c. Ignite the methanol on the asbestos wick and allow to burn for 30 seconds.

d. Invert the stainless steel receiver flask over the funnel and the burning asbestos ring. Leave the flask in place for 15 minutes.

e. Remove the flask and rinse thoroughly with sterile water.

2. Sterilize stainless steel forceps by immersing tips in methanol and passing them through a flame. (Do not hold forceps in flame.) Resterilize forceps before each use. Cool forceps several seconds to prevent scorching of membrane filter.

3. Assemble filtration equipment. Insert filter base into receiver flask, plug the suction tube adapter into the hole on the filter holder base, and connect the opposite end of the suction tube to the syringe inlet valve.

4. Unlock and remove the sterilized funnel and, using sterile forceps, replace a sterile membrane filter (0.7-micrometer pore sized, 47-mm diameter) over the porous plate of the filter base, grid side of the membrane up. Replace funnel on filter base carefully to avoid tearing or creasing the membrane. Apply twist lock.

5. Before any actual samples are run, process a blank sample for each of the media types being used. The blanks need to consist of 20-50 mL of buffer dilution water processed and incubated in the same manner as the actual sample (described below). After incubation, the absence of colonies on the blank plates confirms that contamination of the filtration apparatus as well as the media has not occurred. After the blank plates have been run, the actual sample(s) can be processed.

6. Shake the sample vigorously, at least 25 times, before each volume is withdrawn and immediately withdraw sample volume to be filtered. (Filter the smallest sample volume first.)

If the volume of sample to be filtered is 10 mL or more, transfer the sample with a sterile pipet or graduated cylinder directly into the funnel.

If the volume of sample to be filtered is between 1.0 and 10.0 mL, pour about 10 mL of sterile buffer dilution water into the funnel before pipeting the sample. This procedure facilitates distribution of organisms on the membrane filter.

If the volume of the original water sample to be filtered is less than 1.0 mL, prepare dilutions with sterile buffer-dilution water in sterile milk-dilution bottles and transfer appropriate volume of dilution to the membrane. One of the dilutions in table 8 will probably be applicable:

Table 8.--*Methods of dilution for obtaining small sample volumes*

Dilution (mL)	Volume of sample added to 99 mL sterile dilution water	Equivalent volume (mL) of original sample per mL of dilution
1:10	11.0 mL of original sample	0.1
1:100	1.0 mL of original sample	0.01
1:1000	1.0 mL of 1:10 dilution	0.001
1:10000	1.0 mL of 1:100 dilution	0.0001

NOTE: When preparing dilutions, use a sterile pipet or hypodermic syringe for each dilution. After each transfer between bottles, close and shake the bottle vigorously at least 25 times. Diluted samples are to be filtered within 20 minutes after preparation.

7. After the sample has been transferred to the filter funnel, apply vacuum by pumping the syringe plunger slowly.

8. Rinse side of funnel twice with 20-30 mL of sterile buffer dilution water while applying vacuum.

9. Release vacuum by briefly removing suction tube adapter from hole on filter holder base.

10. Remove the funnel and hold in one hand until membrane filter has been removed.

11. With sterile forceps, remove the membrane filter from the filter base. Replace funnel on filter holder base.

12. Open petri dish and place membrane filter (grid side up) on agar in petri dish. Use a rolling action starting at one edge to avoid trapping air bubbles under the membrane. Inspect the membrane in the petri dish for uniform contact with the agar. If air is trapped under the membrane, remove the membrane and roll on again.

13. Replace top of petri dish and record the time. Invert the petri dish so that the plated membrane filter is upside down.

14. Continue with filtration of the other volumes of samples, in order of increasing sample volume. Record on the field notes the volumes filtered. Rinse the filter funnel with sterile buffer dilution water between filtrations.

15. After the sample volumes have been filtered, place the inverted petri dishes in the preheated oven, incubate, and count as follows:

    a. Total coliform: (22-24 hours at 35°C ± 0.5°C). Remove and count, recording the values for each petri dish on the field form. For total coliform the colonies needs to be dark red with a golden green metallic sheen. The sheen can cover the entire colony or appear in the central area or on the periphery. The counts are best made with the aid of X10 to X15 magnification and a fluorescent illuminator placed directly above the plate.

b. Fecal coliform: (22-24 hours at 44.5°C ± 0.2°C). Remove and count, recording the values for each petri dish on the field form. Counts need to be made within 20 minutes after the plates have been removed from the incubator. Fecal coliform colonies have deep blue color and any that are gray to cream color are not counted. The counts are best made with the aid of X10 to X15 magnification.

c. Fecal streptococci: (48 ± 2 hours at 35°C ± 0.5°C). Remove and count, recording the values for each petri dish on the field form. The colonies may be deep red to pink in color and generally are of a smaller size than the above two types of bacteria colonies. The counts are better made with the aid of X10 to X15 magnification.

If plates of a group have colonies that are in excess of the ideal range, and colonies of another plate(s) are within the range or close, counting the plate having excessive colonies is not necessary.

16. Calculate the number of bacteria colonies per 100 mL of sample as follows:
 a. For colony counts within the ideal range use the following formula:

$$\text{Bacteria colonies per 100 mL} = \frac{\text{Bacteria colonies counted} \times 100}{\text{volume (mL of original sample filtered)}} \qquad (17)$$

 b. If dilutions of the original sample were made before filtration, calculate the volume (milliliters) of the original sample from the following formula:

$$\text{Volume (mL of original sample)} = \text{Volume (mL) of diluted sample filtered} \times \text{Equivalent volume (mL) of original sample per mL of dilution} \qquad (18)$$

Assume for example that a 1:100 dilution was made, that a volume of 10mL of the diluted sample was filtered, and that the colony on the filer was 50. (See table 8).

$$\text{Volume (mL) of original sample} = (10) \times (0.01) = 0.1 \text{ mL} \qquad (19)$$

and

$$\text{Bacteria colonies per 100 mL} = \frac{50 \times 100}{0.1} = 50{,}000 \qquad (20)$$

 c. Counts less than the ideal of 20 colonies or greater than the maximum listed for each bacteria type are calculated and reported as the number of colonies per 100 mL, followed by the statement "Estimated count based on nonideal colony count" or by an appropriate remarks code.

d. If no filter develops characteristic colonies, calculate assuming that the largest sample volume filtered had one bacteria colony.

For example, if the largest sample filtered was 25 mL, and no bacteria colony was found, calculate assuming one colony as follows:

$$\text{Colonies per 100 mL} < \frac{1 \times 100}{25} \text{ or } < 4 \qquad (21)$$

Report: "< 4 colonies per 100 mL. Estimated count based on nonideal colony count" or by an appropriate remarks code.

e. If all filters bear colonies too numerous to count, a minimum estimated value can be reported by assuming a maximum count within the ideal count range on the smallest volume filtered (total coliform-80, fecal coliform60, fecal streptococcus-100). For example, if the smallest sample volume filtered was 1 mL, and more than 80 total coliform colonies developed on the filter, calculate as follows:

$$\text{Coliform colonies per 100 mL} > \frac{80 \times 100}{1} \text{ or } > 8{,}000$$

Report > 8,000 colonies per 100 mL "Estimated count based on nonideal colony count."

f. Sometimes, two or more filters of a series will produce colony counts within the recommended range. The method of calculating and averaging is as follows:

$$\begin{array}{ll} \text{Volume 1 (mL)} & \text{Colony count for filter 1} \\ \underline{\text{+ volume 2 (mL)}} & \underline{\text{+ colony count for filter 2}} \\ \text{Volume, sum (mL)} & \text{Colony count, sum} \end{array} \qquad (22)$$

$$\text{Bacteria colonies per 100 mL} = \frac{\text{Colony count, sum} \times 100}{\text{Volume, sum (mL)}} \qquad (23)$$

NOTE: Do not calculate the colonies per 100 mL for each filter and then average the results.

For example, assume that sample volumes of 1, 5, 20, and 100 mL were filtered and that the total coliform colony counts for the 5-mL and 20-mL samples were 20 and 75, respectively. Calculate as follows:

Volume filtered	Colony count
5 mL	20
+ 20 mL	+ 75
25 mL	95

$$\text{Colonies per 100 mL} = \frac{95 \times 100}{25} = 380$$

g. Water samples with a large concentration of suspended sediment may preclude the filtration of adequate sample volumes to produce the ideal number of colonies. Under such circumstances a sample volume may be divided into two or more portions and filtered through separate membrane filters.

For example, assume that the sediment content precludes the filtration of more than 5 mL of a sample (that is, the accumulation of sediment on the membrane filter prevents the development of colonies.) However, past analyses indicate that water from the site usually contains 100-200 colonies per 100 mL. Filter four or five 5-mL portions of the sample through separate membrane filters and calculate as follows:

Sample volume (mL)	Colony count
5 (first filter)	6
5 (second filter)	10
5 (third filter)	8
5 (fourth filter)	6
20 (total volume)	30 (total colonies)

$$\text{Colonies per 100 mL} = \frac{30 \times 100}{20} = 150$$

Fortunately, experience has shown that samples containing large amounts of sediment also contain large amounts of bacteria, especially coliform. Therefore, at some sites, a diluted sample may be used to eliminate the interference of the sediment concentration.

17. After the appropriate calculations, report the number of colonies to whole numbers for values less than 100 and to two significant figures for values of 100 and greater.

18. After counting and before discarding, the bacteria plates are to be autoclaved at 121°C (250°F) and 15 lb/in^2 for 15 minutes.

REAGENTS FOR FIELD DETERMINATIONS

Preparation of some of the reagents for field determinations outlined in this manual have been described previously. These and other reagents utilized for field determinations and the methods of preparation are listed in the following tabulations.

When the chemicals to be used for the preparation of these reagents are received, they need to be dated and stored in dust-free cabinets or dessicators, or refrigerated as appropriate. When the reagents are prepared, label with the date prepared and the initials of the analyst(s).

These reagents can be prepared by the District water-quality personnel, ordered from the central laboratory, or ordered from commercial suppliers. Medium for bacteriological determinations will be prepared as needed by field service units.

Specific conductance

Potassium chloride solution, 0.00702N.--Dissolve 0.5232 g KCl, dried at 180°C for 1 hour, in demineralized water and dilute to 1,000 mL (also available from the Denver Central Laboratory).

pH

Standard buffer solutions, pH 4.0, 7.0, and 10.0--Prepared buffers from a commercial supplier. (See section "Field-measurement methods--pH--pH buffers.")

Carbonate and bicarbonate

1. Sodium carbonate standard solution, 1.00 mL = 1.00 milligram HCO_3. -- Dry 1.0 g primary standard Na_2CO_3 at 150°-160°C for 2 hours. Cool in a desiccator and dissolve exactly 0.8686 g in a carbon-dioxide-free, demineralized water; dilute to 1,000 mL.

2. Sulfuric acid standard solution, 0.01639 N, 1.00 mL = 1.00 mg HCO_3.--Add 0.5 mL concentrated H_2SO_4 (specific gravity 1.84) to 950 mL demineralized water. After the solution has been thoroughly mixed, standardize it by titrating 25.0 mL Na_2CO_4 (1.00 mL = 1.00 mg HCO_3) to pH 4.5. Adjust the concentration of the sulfuric acid standard solution to exactly 0.01639 N by dilution with demineralized water or by addition of dilute acid as indicated by the first titration. Confirm the exact normality by restandardization. Although the sulfuric acid solution is reasonably stable, its normality needs to be verified at least monthly.

3. Carbon-dioxide-free demineralized water.--Prepare fresh as needed by boiling demineralized water for 15 minutes and cooling rapidly to room temperature. Cap the bottle in which the water has been boiled with a slightly oversize inverted beaker to minimize entry of carbon dioxide from the atmosphere during the cooling process.

Bacteria

1. Buffered dilution water.--See section "Field-measurement methods--Bacteriological analyses--Buffered dilution water."

2. Sodium hydroxide solution 1N.--Dissolve 40.0g NaOH in demineralized water and dilute to 1 liter.

3. Ethyl alcohol solution, 2 percent.--Add 20 mL of 95 percent ethyl nondenatured alcohol to 1 liter of demineralized water. Store in refrigerator.

4. M-Endo agar medium.--See section "Field-measurement methods--Total coliform bacteria--Membrane-filter method--Preparation of M-Endo agar medium."

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SUPPLEMENTAL INFORMATION

Included in this section are examples of forms and instructions that are used in the field to record data for entry into WATSTORE (National Water Data Storage and Retrieval System of the U.S. Geological Survey) and for sending samples to the Geological Survey Central Laboratory.

(p. 81 follows)

BACTERIOLOGY

Time Collected ________________

Time Filtered ________________

Collect. Station	Fec Coli Vol	Fec Coli Cnt	Fec Strp Vol	Fec Strp Cnt	Tot Coli Vol	Tot Coli Cnt
Col/100ml Remarks						
Ideal cnt Incub. T. Time(hrs)	20-60 44.5°C 20-24		20-100 35°C 46-50		20-80 35°C 22-24	

Col/100 ml = $\frac{\text{100 x Col. Counted}}{\text{ml of sample filt.}}$

TEMPERATURE RECORDER

☐ Tape Removed
Stream Temp ____________
Recorder Temp ____________

☐ Tape Started
Stream Temp ____________
Recorder Temp ____________

☐ Recalibrated

INSTRUMENT CALIBRATION

Parm	Mtr W#	Std/Mtr	Std/Mtr	Std/Mtr
pH				
SC				

REMARKS:

DISSOLVED OXYGEN

PAO Normality =	1	2
Final buret reading		
Initial buret reading		
Titrant used (A)		
Vol. of sample (B)		
D.O.(mg/L)=A X 200/B		

Bar P = _______ Temp = _______ °C

DO Sat = _______ Cond K = _______

DO Sat X Cond K = Cor DO Sat______

% Sat= $\frac{\text{(DO)}}{\text{(Cor DO Sat)}}$ X 100=_____

ALKALINITY

H_2SO_4 Normality ________________

Normality Factor (K)	1	2
Initial pH		
Buret at pH 8.3		
Buret at pH 4.5		
Initial buret read.		
Titrant used (A)		
Vol of sample (B)		
Alk=(1000/B)X(A)X(K)		

PERIPHYTON

Location	No. Place	Date In	No. Recov	Date Out

U.S. GEOLOGICAL SURVEY, WRD
WATER QUALITY FIELD NOTES

Station Name ____

Station No. ____________________ Date ________ Time ________

Party Name ____________________ Project No. ____________

FIELD MEASUREMENTS

Gage HT (00065)______ft.
Q, Inst (00061)______CFS { Meas Rate Est
Temp. Water (00010)______°C
Temp. Air (00020)______°C
Sp. Cond. (00095)______umho 25°C
pH (00400)______units
Dis Oxy (00300)______mg/L
DO % Sat. (00301)______%
Alkalinity (00410)______mg/L
HCO_3 (00440)______mg/L
CO_3 (00445)______mg/L
Fecal Coli (31625)______Col/100 ml
Fecal Strep (31673)______Col/100 ml
Baro Press (00025)______mm Hg

SAMPLES COLLECTED

(Circle) Monthly, Quarterly, High, Medium, Low Flow

Schedules__________, __________
__________, __________

Nutrients -------------- N ☐ P ☐
Major Ions -------------------- ☐
Trace Elements--Non Filt ☐ Filt ☐
BOD-- ☐ COD-- ☐ TOC-- ☐
DOC-- ☐ SOC-- ☐ Vol Filt____ml
Pesticide -------- Bed ☐ Water ☐
Sediment --- X-Sec ☐ DS ☐ Bed ☐
Radiochemical ----------------- ☐
Periphyton -------------------- ☐
Phytoplankton ----------------- ☐
X-Section Survey (Reverse) ---- ☐

SAMPLING CONDITIONS

SAMPLE LOCATION: Wading, Cable, Ice, Boat, Bridge, ______ Feet, Mile, Above, Below, Gage and ________________________ Pool, Riffle, Open Channel, Braided, Backwater, Sand, Rock, Mud Bottom

SAMPLE METHOD: EDI, EWI, Single Vertical, Point, Surface

COLLECTION POINTS: __________, __________, __________, __________,
__________, __________, __________, __________,
__________, __________, LB=________, RB=________,
Width=__________

SAMPLER TYPE: Chemical______Sediment______DO______Bed______
Bacteria______(Sterilized ☐)

STREAMFLOW (01351): Dry, Low, Normal, Above Normal, Flood, Ice Cover___%

WEATHER DATA: Weather Code (00041)____, % Cloud Cover (00032)____
Wind Speed MPH (00035)____

WEATHER CODES

0 - CLOUDLESS
1 - PARTLY CLOUDY
2 - CLOUDY
3 - OVERCAST
10 - PRECIPITATION WITHIN SIGHT
13 - UGLY, THREATENING SKY
40 - FOG
50 - DRIZZLE
51 - SLIGHT DRIZZLE, INTERMITTENT
52 - SLIGHT DRIZZLE, CONTINUOUS
53 - MODERATE DRIZZLE, INTERMITTENT
54 - MODERATE DRIZZLE, CONTINUOUS
55 - THICK DRIZZLE, INTERMITTENT
56 - THICK DRIZZLE, CONTINUOUS
57 - DRIZZLE AND FOG
58 - SLIGHT OR MODERATE DRIZZLE AND RAIN
59 - THICK DRIZZLE AND RAIN
60 - RAIN
61 - SLIGHT RAIN, INTERMITTENT
62 - SLIGHT RAIN, CONTINUOUS
63 - MODERATE RAIN, INTERMITTENT
64 - MODERATE RAIN, CONTINUOUS
65 - HEAVY RAIN, INTERMITTENT
66 - HEAVY RAIN, CONTINUOUS
67 - RAIN AND FOG
68 - SLIGHT OR MODERATE MIXED RAIN AND SNOW
69 - HEAVY MIXED RAIN AND SNOW
70 - SNOW OR SLEET
71 - SLIGHT SNOW IN FLAKES, INTERMITTENT
72 - SLIGHT SNOW IN FLAKES, CONTINUOUS
73 - MODERATE SNOW IN FLAKES, INTERMITTENT
74 - MODERATE SNOW IN FLAKES, CONTINUOUS
75 - HEAVY SNOW IN FLAKES, INTERMITTENT
76 - HEAVY SNOW IN FLAKES, CONTINUOUS
77 - SNOW AND FOG
78 - GRANULAR SNOW (FROZEN DRIZZLE)
79 - ICE CRYSTALS
80 - SHOWER(S)
81 - SLIGHT OR MODERATE RAIN SHOWER(S)
82 - HEAVY RAIN SHOWER(S)
83 - SLIGHT OR MODERATE SNOW SHOWER(S)
84 - HEAVY SNOW SHOWER(S)
85 - SLIGHT OR MODERATE RAIN AND SNOW SHOWER(S)
86 - HEAVY RAIN AND SNOW SHOWER(S)
87 - GRANULAR SNOW SHOWER(S)
88 - SLIGHT OR MODERATE HAIL OR RAIN AND HAIL SHOWER(S)
89 - HEAVY HAIL OR RAIN AND HAIL SHOWER(S)
90 - THUNDERSTORM
93 - SLIGHT THUNDERSTORM WITH RAIN OR SNOW
94 - SLIGHT THUNDERSTORM WITH HAIL
95 - MODERATE THUNDERSTORM WITH RAIN OR SNOW
96 - MODERATE THUNDERSTORM WITH HAIL
97 - HEAVY THUNDERSTORM WITH RAIN OR SNOW
99 - HEAVY THUNDERSTORM WITH HAIL

ALKALINITY

INCREMENTAL TITRATION

pH	milliliters of acid or digital counter value

Titrant Normality______________N

WATSTORE/LAB CODES

	Watstore	Lab Code
Gage Height	00065	332
Streamflow, Inst (CFS)	00061	61
Temperature, Water	00010	64
Temperature, Air	00020	65
Specific Conductance	00095	21
pH	00400	51
Dissolved Oxygen	00300	25
DO, % Saturation	00301	26
Alkalinity	00410	2
HCO_3	00440	8
CO_3	00445	14
Fecal Coliform	31625	97
Fecal Strep	31673	98
Barometric Pressure	00025	1167
Weather	00041	208

X-SECTION SURVEY

Station										
Temp.										
Cond.										
DO										
pH										

CENTRAL LABORATORIES ANALYTICAL SERVICES REQUEST FORM

Special Handling (Circle as appropriate and explain in record 5)

Hazardous material

Field ID ______

Site Type (circle one)

SW - Surface Water
GW - Ground Water
ME - Meteorological

LK - Lake
ES - Estuary
SP - Spring
SS - Special Source

Station Name	Field Office	Project	Collector	Phone (FTS)

File Deposition*
(Circle one)
Q - WATSTORE
X - Lab File

For Laboratory Use Only

Record 1 — Sample identification

Station ID or Unique Number* ______

Project Account # ______

1 9									
Year*	Month*	Day*	Time*	Month	Day	Time	State Code*	District/ User Code*	County Code
Begin Date				Composite End Date					

Record 2 — Analysis level codes and schedules

		H or 9				
Sample Medium**	Geologic Unit	Analysis Status**	Analysis Source**	Hyrdologic Condition**	Sample Type**	Hydrologic Event**

Schedule #1	Schedule #2	Schedule #3	Schedule #4	Schedule #5

Record 3 — Laboratory codes to be added to (A) or deleted from (D) above schedules

Code	A/D	Code	A/D	Code	A/D	Code	A/D	Code	A/D	Code	A/D	Code	A/D	Code	A/D
Code	A/D	Code	A/D	Code	A/D	Code	A/D	Code	A/D	Code	A/D	Code	A/D	Code	A/D

Record 4 — Field values to be added to analysis.

WATSTORE/ Lab Code	Value	Rmk Code	QA Code	Meth Code	WATSTORE/ Lab Code	Value	Rmk Code	QA Code	Meth Code	WATSTORE/ Lab Code	Value	Rmk Code	QA Code	Meth Code
00027/ 83 Collecting Agency					82398/1201 Sampling Method Code					00061/ 61 Discharge, Instantaneous (cfs)				
72019/ 312 Depth to Water (BLS) (ft)					00020/ 65 Air Temperature (°C)					00010/ 64 Water Temperature (°C)				
00095/ 21 Specific Conductance (umhos)					00400/ 51 pH, Field					00025/1167 Barometric Pressure (mm Hg)				
00300/ 25 Dissolved Oxygen (mg/L)					00410/ 2 Alkalinity, Field (mg/L)					/				
/					/					/				

Records 5, 6 — Comments (limit to 138 characters)

Record 5 ______

Record 6 ______

Total number of sample bottles for this request: ______

* – Mandatory for acceptance for laboratory analysis
** – Mandatory for storage in WATSTORE

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ANALYSIS LEVEL AND PARAMETER LEVEL CODES

SAMPLE MEDIUM CODES

A – Artificial
B – Solids (street sweepings, etc.)
C – Animal tissue
D – Plant tissue
E – Core material
F – Interstitial water
G – Soil
H – Bottom material
J – Sludge
K – Soil moisture
L – Phytoplankton (species & count)
M – Phytoplankton (species)
N – Periphyton (species)
O – Benthic invertebrates (species & count)
P – Periphytic diatoms (species & count)
1 – Intragravel water
2 – Leachate
3 – Dry deposition
4 – Landfill effluent
5 – Elutriation
6 – Ground water
7 – Wet deposition
8 – Bulk deposition
9 – Surface water

HYDROLOGIC CONDITION CODES

4 – Stable, low stage
5 – Falling stage
6 – Stable, high stage
7 – Peak stage
8 – Rising stage
9 – Stable, normal stage

HYDROLOGIC EVENT CODES

A – Spring breakup
B – Under ice cover
C – Glacial lake outbreak
D – Mudflow
E – Tidal action
H – Dambreak
J – Storm
1 – Drought
2 – Spill
3 – Regulated flow
4 – Snowmelt
5 – Earthquake
6 – Hurricane
7 – Flood
8 – Volcanic action
9 – Routine sample

ANALYSIS STATUS CODES *

H – Initial entry
9 – Proprietary data **

ANALYSIS SOURCE CODES *

1 – USGS lab and non-USGS field
2 – USGS lab and non-USGS lab
3 – USGS lab and non-USGS lab and field
4 – USGS lab and field and non-USGS field
5 – USGS lab and field and non-USGS lab
6 – USGS lab and field and non-USGS lab and field
8 – USGS lab
9 – USGS lab and field

SAMPLE TYPE CODES

H – Composite (time)
1 – Spike
3 – Reference
5 – Duplicate
7 – Replicate
9 – Regular

REMARK CODES *

Blank – Not remarked
E – Estimated
1 – Less than
2 – Greater than

QUALITY ASSURANCE CODES *

G – Non-USGS field value, in review
I – USGS field value, in review
7 – Non-USGS field value, proprietary **
9 – USGS field value, proprietary **

VALUES FOR PARAMETER CODE 82398

10.00 – EWI
20.00 – EDI
30.00 – Single vertical
40.00 – Multiple verticals
50.00 – Point sample
60.00 – Weighted bottle
70.00 – Grab sample (Dip)
100.00 – Van Dorn bottle
110.00 – Sewage sampler
4010.00 – Thief sampler
4020.00 – Bailer
4030.00 – Suction pump
4040.00 – Submersible pump
4050.00 – Squeeze pump
4060.00 – Gas reciprocating pump
4070.00 – Air lift
4080.00 – Peristaltic pump
4090.00 – Jet pump
4100.00 – Flowing well
8010.00 – Other

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* Additional codes for post-processing water-quality records are available in the WATSTORE documentation.

** Designation of proprietary data requires permission from Regional Hydrologist's office.

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INSTRUCTIONS FOR COMPLETING ANALYTICAL SERVICES REQUEST FORM

RECORD 1 – SAMPLE IDENTIFICATION

* File Deposition – Circle 'WATSTORE' or 'Lab File'.
Lab ID – Leave blank (for laboratory use only).
* ID Number – Enter downstream order number, 15 digit latitude, longitude and sequence number, or unique number.
* Begin Date (year) – Enter 2 digit number for year sample collection started.
* Begin Date (month) – Enter 2 digit number for month sample collection started.
* Begin Date (day) – Enter 2 digit number for day sample collection started.
* Begin Date (time) – Enter 4 digit military time sample collection started.
End Date (month) – Enter 2 digit number for month sample collection ended.
End Date (day) – Enter 2 digit number for day sample collection ended.
End Date (time) – Enter 4 digit military time sample collection ended.
* State Code – Enter 2 digit FIPS code for State in which station is located.
* District Code – Enter 2 digit District code followed by a 1 digit subdistrict code (when implemented) to indicate which office all sample data, charges, and billing information are to be routed.
County Code – Enter 3 digit FIPS code for county in which station is located.
Project Account – Enter 9 digit account number (omit when unique number is used).

RECORD 2 – ANALYSIS CODES AND SCHEDULES

** Sample Medium – Enter sample medium code (see attached table).
Geologic Unit – Enter geologic unit for ground-water sample (multiple aquifer identification).
** Analysis Status – Circle 'H' (initial entry) or '9' (proprietary data).
** Analysis Source – Enter analysis source code (see attached table).
** Hydrologic Condition – Enter hydrologic condition code (see attached table).
** Sample Type – Enter sample type code (see attached table).
** Hydrologic Event – Enter hydrologic event code (see attached table).
Schedules – Enter schedules desired. Up to five schedules may be requested as long as the total analysis does not exceed 120 parameters. If no schedule is requested then enter 0 for the first schedule. Do not include schedule numbers called for by a unique number.

RECORD 3 – LABORATORY CODES TO BE ADDED OR DELETED FROM ABOVE SCHEDULES

Lab code – Enter lab code for parameters to be added or deleted. Enter 'A' for addition or 'D' for deletion.

RECORD 4 – FIELD VALUES TO BE ADDED TO ANALYSIS

Value, Remark, Quality Assurance, and Method – Enter value, remark code and quality assurance code. Precision codes are assigned from parameter code dictionary by laboratory computer. Method code will be developed at a later date.

RECORDS 5, 6 – COMMENTS

Record 5
Record 6 – Comments to laboratory should be made in record 5; otherwise, comment fields 5 and 6 may be filled in at the discretion of the user.

---

* Mandatory for acceptance for laboratory analysis.

** Mandatory for storage in WATSTORE.

3rd printing

SIGNIFICANT FIGURES CHART

CONSTITUENT	watstore code	lab code					
Sample depth (feet)	00003	79	.XX	X.XX	XX.X	XXX	XXXO
Water Temp (to nearest 0.5 C)	00010	64	.X	X.X	XX.X	XXX	XXXO
Air Temp (to nearest 0.5 C)	00020	65	.X	X.X	XX.X	XXX	XXXO
Barometric Pressure	00025	1167	--	X	XX	XXX	XXXO
Collecting agency	00027	83	--	X	XX	XXX	XXXX
Weather	00041	208	--	X	XX	XXX	XXXO
Instantaneous discharge	00061	61	.XX	X.X	XX	XXX	XXXO
Conductance	00095	21	--	X	XX	XXX	XXXO
Sample depth (meters)	00098	none	.XX	X.X	XX.X	XXX	XXXO
Dissolved Oxygen	00300	25	.X	X.X	XX.X		
pH	00400	51	.X	X.X	XX.X		
Alkalinity	00410	2	.X	X.X	XX	XXX	XXXO
Bicarbonate	00440	8	--	X	XX	XXO	XXXO
Carbonate	00445	14	--	X	XX	XXO	XXXO
Fecal Coliform	31625	97	--	X	XX	XXO	XXOO
Fecal Strep	31673	98	--	X	XX	XXO	XXOO

For portions of the field form where calculations are required, the exact value of the calculation is to be given. When the value is transfered to the "FIELD MEASUREMENT" column, the proper rounding is to be done; that is, any value in the "FIELD MEASUREMENT" column is to be rounded according to the above rules.

When reporting additional field values; that is, parameters not already preprinted on the form, be sure to use both the WATSTORE code and the Laboratory code. It is very time consuming for the laboratory keypunchers to have to look up these codes.